University of Alberta Library
0 1620 3711540 7

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex libris
universitatis
albertaensis

A Study of the Effect of Concentration, Pressure, Temperature, and Added Sulphur Compounds on the Corrosion of Lead in Sulphuric Acid.

Digitized by the Internet Archive
in 2018 with funding from
University of Alberta Libraries

https://archive.org/details/studyofeffectofc00badn

T H E S I S

A STUDY OF THE EFFECT OF CONCENTRATION, PRESSURE, TEMPERATURE, AND ADDED SULPHUR COMPOUNDS ON THE CORROSION OF LEAD IN SULFURIC ACID.

Part I. The Effect of Sulfuric Acid on Lead under High Pressure.

Part II. The Action of Sulfur Dioxide and Hydrogen Sulfide on Lead Immersed in Sulfuric Acid.

Part III. The Corrosion of Lead by Sulfuric Acid in Desulfurizing Gas Pressure Scrubbers.

Submitted in partial fulfilment of
the requirements for the degree of
Master of Science.

by

JOHN F. BADNER

April, 1935. Department of Chemistry, University of Alberta. Edmonton, Alberta.

CONTENTS

		Page
General Introduction		1
Part I.	THE EFFECT OF SULFURIC ACID ON LEAD UNDER HIGH PRESSURE	
1.	Introduction	4
2.	Literature review	5
3.	Experimental	9
	a. Materials used	9
	b. Apparatus	10
	c. Analytical procedure	11
4.	Results and discussion	16
5.	Conclusions and summary	38
Part II.	THE ACTION OF SULFUR DIOXIDE AND HYDROGEN SULFIDE ON LEAD IMMERSED IN SULFURIC ACID	
1.	Introduction	40
2.	Literature review	41
3.	Experimental	44
	a. Materials used	44
	b. Apparatus	44
	c. Analytical procedure	44
4.	Results and discussion	46
5.	Conclusions and summary	58

(Continued on next page.)

Contents (Continued)

Page

Part III. THE CORROSION OF LEAD BY SULFURIC ACID IN DESULFURIZING GAS PRESSURE SCRUBBERS

1. Introduction 59

2. Literature review 60

3. Experimental 64

a. Materials used 64

b. Apparatus 64

c. Analytical procedure 66

d. Determination of Sulfur in Gas. 70

4. Results and discussion 74

5. Summary and conclusions 91

General discussion 93

General conclusions and summary 95

Acknowledgement 96

References 97

- - - - -

Illustrations and Graphs

Illustrations — Page

Plate 1.- The laboratory 1

Plate 2 - Hydraulic pressure equipment 8

Plate 3 - Analytical laboratory 39

Plate 4 - Research apparatus 63

Fig. 1 - Hydraulic apparatus 12

Fig. 2 - Reaction vessel (pressure) 14

Fig. 3 - Reaction vessel (atmospheric) 43

Fig. 4 - Gas pressure apparatus 64

Fig. 5 - The autoclave 67

Fig. 6 - Apparatus used to determine S in gas ... 69

Fig. 7 - Data of Tables I, and I(a) 21

Fig. 8 - Data of Table II 24

Fig. 9 - Data of Table III 27

Fig. 10 - Data of Table IV 30

Fig. 11 - Data of Table V 33

Fig. 12 - Data of Table VI 50

Fig. 13 - Data of Table VII 54

Fig. 14 - Data of Table X 78

Fig. 15 - Data of Table XI 82

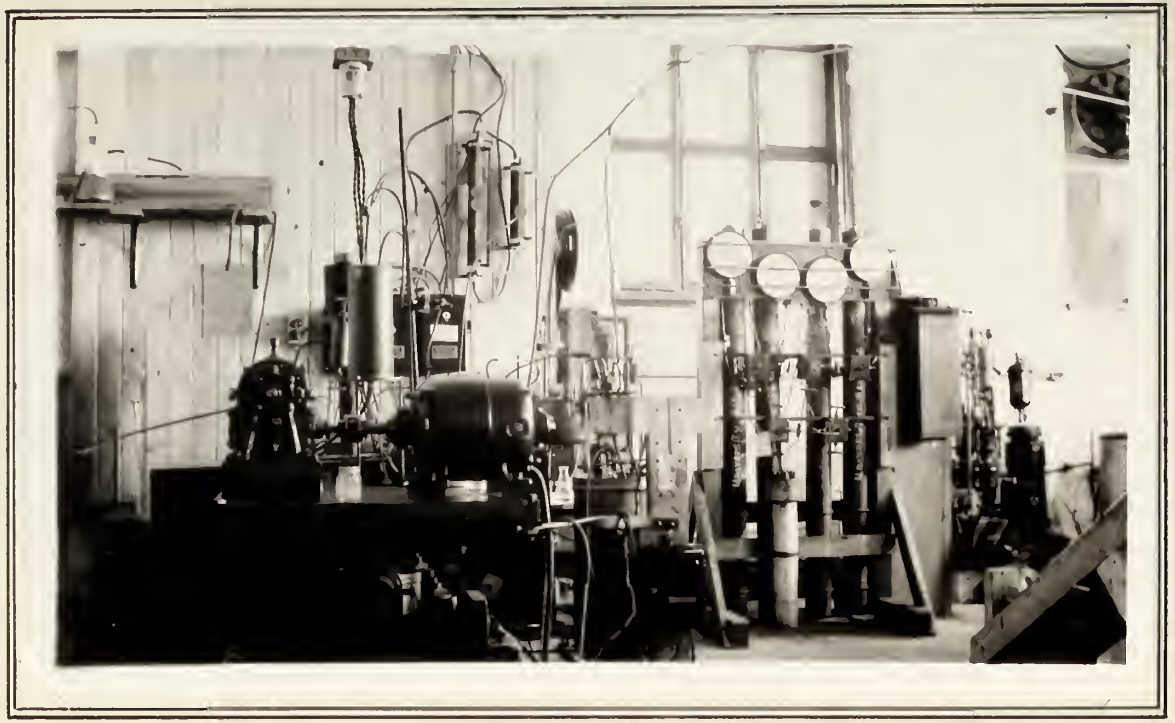
Fig. 16 - Data of Table XII 86

Fig. 17 - Composite data of 93% acid 89

- - - - -

PLATE 1

General view of the apparatus used in Part 1 and Part 111. Motor and gear of hydraulic pump in left foreground, thermostat in centre foreground, main gas storage and gas compressor in right background.



General Introduction

This research was suggested by observations on the rapid corrosion of lead gaskets used to seal high pressure gas scrubbers containing concentrated sulfuric acid. These scrubbers are used to remove sulfur compounds added as odorants to Viking natural gas supplied to the city, and used extensively in gas research here. Considerable amounts of sulfur dioxide were evident in the off-gases from these scrubbers. The sulfur dioxide was removed by sodium hydroxide. Apart from its purely local interest, this work is of value as a contribution to the general study of the activity of acids under high pressure. The investigation was planned, primarily, to supply an explanation for the observations made on the corrosion of lead gaskets, and necessarily included experimental work on the corrosion of lead in sulfuric acid of various strengths, under various pressures and temperatures. A complete program would have included the activity of sulfur dioxide and hydrogen sulfide solutions under pressure. The lack of time and facilities has not permitted more than a beginning in this last respect by including work at atmospheric pressure only.

Consideration of the problem showed that in preliminary work at least, three main divisions were necessary. First - there was the determination of the action of sulfuric acid alone

in various concentrations and at various pressures upon metallic lead. This part includes logically the effect of temperature. Second - there was the action of solutions of sulfur dioxide and hydrogen sulfide in sulfuric acid of various concentrations on metallic lead. This part was limited to work at atmospheric pressure and room temperature. Third - quantitative determinations of corrosion of lead under controlled conditions simulating those obtaining in the scrubbers, was carried out. This involved the determination of the sulfur content of the gas before and after passage through the acid, its conversion to sulfur dioxide or hydrogen sulfide, if any, and the amount retained by the acid in solution or in combination.

It has been accepted generally that the activity or strength of acids, and particularily acid gases, in solution, increases markedly with pressure. The work of Krase (8) may be cited for example. Krase showed that saturated solutions of carbon dioxide under a pressure of 100 atmospheres had an increase in dissociation constant from something like 10^{-7} to 10^{-5}.

In regard to the corrosion of lead in sulfuric acid at atmospheric pressure, a large volume of publications has appeared showing little agreement, either as to the rate of corrosion, the mechanism of reaction, or the solubility of lead sulfate.

In this work, lead sulfite is also a factor and little appears in the literature in regard to the properties of this compound. It may be assumed that the process of corrosion is normal and follows the electrolytic theory as advocated by W. R. Whitney (16) J. W. Shipley (15), B. Lambert and H. E. Cullis (9), and others. Little more can be said without further collection and study of experimental data.

PART 1

The Effect of Sulfuric Acid on Lead under High Pressures.

PART 1

Introduction

As already stated, it was considered of interest to make some observations on the effect of various strengths of sulfuric acid on lead, under varying conditions of temperature and pressure. Such work was not new excepting in regard to the use of high pressures. It was necessary, however, to carry out a series of tests under atmospheric conditions as controls, with the same metal and acid for comparative purposes. Lead and sulfuric acid vary in degree of purity, depending on the source of material and the method of manufacture.

The object of this part of the work was, primarily, to determine whether sulfuric acid alone was able to corrode lead at the rate and in the manner originally observed in the high pressure scrubbers.

It was felt that if the number of concentrations of acid were increased in the experiments under atmospheric pressure, that some observations of general nature might be added to this particular field of research. Accordingly, besides the concentration of acid used in the scrubbers, namely 93%, several other concentrations were used - from 37% upwards.

Literature Review

In reviewing the comparatively voluminous literature in connection with lead and sulfuric acid, it is quite evident that no definite agreement has been reached as to the rate and extent of solubility of lead sulfate in sulfuric acid of varying concentrations. But there seems to be adequate reason to believe that the rate of solubility of lead sulfate in sulfuric acid depends on the concentration. In general, it was found that the higher the concentration the greater the solubility of the lead sulfate.

H. Ditz and F. Kanhauser (1) working with concentrated and fuming acids at 17° - 18.5° found the following solubility results:

H_2SO_4%	98.11,	98.94,	100.0,	100.01(5 SO_3),	105.05(15%SO_3)
$PbSO_4$%	0.54	1.34	1.4	3.54	8.23

A. Marshall (10) found 98% H_2SO_4 dissolved 0.09% $PbSO_4$ and
94% H_2SO_4 dissolved 0.06% $PbSO_4$.

J. H. Gladstone and W. Hibbert (5) working with 29% H_2SO_4 (sp. gr. 1.22) claim a solution of 0.012 grams per litre.
C. R. Fresenius (3) found solubility of lead sulfate in dilute H_2SO_4 to be 0.0025 parts per 100 parts acid. Pleisner (14) in his work with dilute acids and water showed that solubility decreased from 0.000126 mols. per 1000 gm. in pure water to 0.000017 per 1000 gm. in 0.005 mols. sulfuric acid.

J. Kolb/(7) reports the following at room temperature:

H_2SO_4 sp. gr. 1.84 dissolves 0.039 gm. $PbSO_4$ per 100 gm. acid
H_2SO_4 sp. gr. 1.793 dissolves 0.011 gm. $PbSO_4$ per 100 gm. acid
H_2SO_4 sp. gr. 1.54 dissolves 0.003 gm. $PbSO_4$ per 100 gm. acid

These and other workers show general agreement, at least, even though greatly at variance with each other in their data. The essential point brought out by this work is the rapid increase in solubility of lead sulfate as the acid concentration approaches 100% and over.

The reaction between lead and sulfuric acid may be assumed to be as follows:

$$Pb + H_2SO_4 = Pb(HSO_4)_2 + H_2$$

The lead acid sulfate, on hydrolysis, forms the normal lead sulfate ($PbSO_4$), which precipitates as a white solid when the solution becomes saturated, or diluted by addition of water. This accounts for the resulting milkiness when water is added to a sulfuric acid solution containing lead sulfate.

Considerable doubt has been expressed as to the composition of the solids formed by the reaction of H_2SO_4 on lead, and the compound $H_2SO_4.PbSO_4$ has been suggested. An investigation of the ternary system, $PbSO_4.H_2SO_4.H_2O$ by A. D. Donk (2) failed to confirm the existance of this compound. According to Donk the only solid phase was $PbSO_4$.

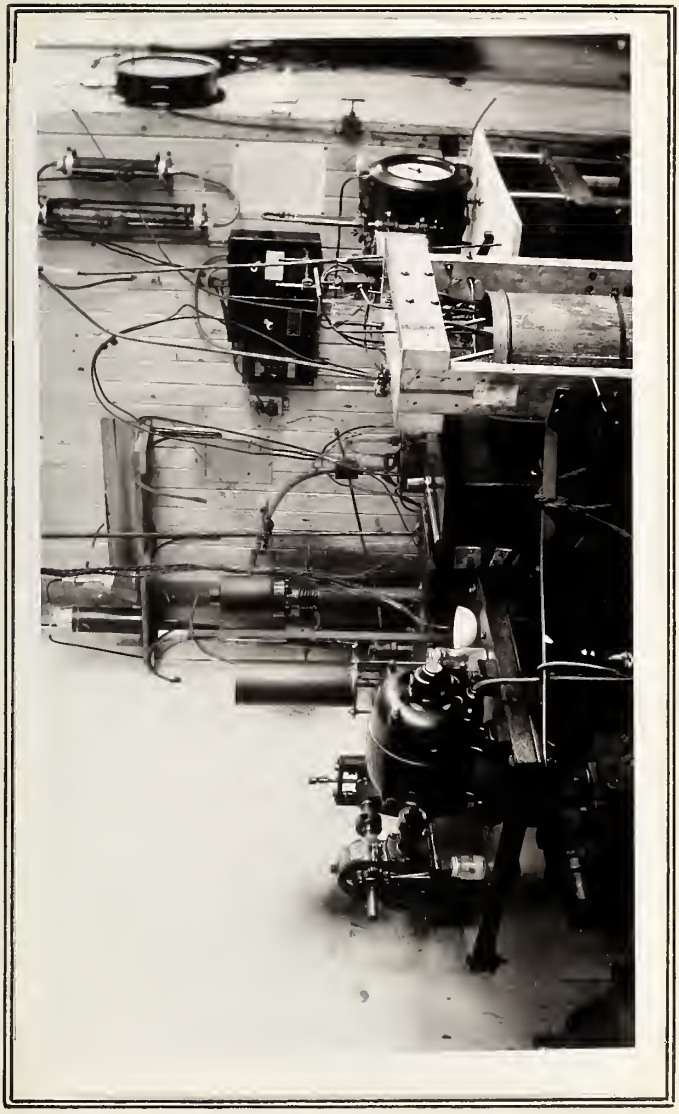
Fuming sulfuric acid attacks lead more rapidly than

sulfuric acid itself. H. Ditz and F. Kanhauser (1) offer the explanation that the more soluble pyrosulfate salt is formed -

$$Pb + H_2S_2O_7 = PbS_2O_7 + H_2$$

PLATE 2

Showing the hydraulic pressure equipment; the thermostat, and apparatus as shown in Figure IV.



Expirmental

Materials

The lead used throughout this experimental work was taken from the same piece of electrolytic lead used for commercial purposes, as manufactured at Trail, B.C. The sample appeared to be of good quality, and was free from visible inclusions. It was not analysed except qualitatively, showing a trace of arsenic and antimony.

The sulfuric acid, (also from Trail B.C.), used in the experiments was drawn directly from a carboy and stored in glass stoppered bottles to serve for the entire set of experiments. This acid had a specific gravity of 1.830, corresponding to a concentration of 93.1% by weight.

The lead samples were cut as nearly as possible the same size - 1.25 in. x 0.25 in. x 0.125 in., to give a surface area of one square inch. Each piece of lead had the oxide coating carefully and thoroughly removed by an abrasive. A hole was punched near one end to facilitate the removal of the lead from the acid, or for suspending the metal in the solution.

Redistilled mercury, further purified by aeration in a 5-10% nitric acid solution, was used as a liquid seal. No noticeable attack by sulfuric acid on the mercury was ever obtained.

Apparatus

The high pressure apparatus for carrying out the determinations is shown diagramatically in Fig. 1. It consisted of a high pressure hydraulic pump, B, capable of operating at pressures of 5,000 lbs. per sq. inch. The pump was connected to a two-way valve, C. From C, connections were made to a relief valve, D, and to the oil reservoir, A. D, was connected to the surge bottle, E, which in turn was connected to a recording Bourdon-tube guage, G, and to the autoclave, F. The autoclave, F, which is shown in detail in Fig. 5, contained the glass reaction vessel, as shown in detail in Fig. 2. The autoclave was immersed in a thermostatically-controlled oil bath, K, the mercury-filled thermoregulator, H, controlling the heater, L, through suitable relays.

The reaction vessel, Fig. 2, was constructed of pyrex glass. The hollow stopper, B, with a glass hook on its lower end, fitted snugly through a ground glass joint. A mercury container, E, was connected to the acid container, C, by means of three wire hooks. The whole was suspended from the head of the autoclave by a wire, A. The lead sample was hung on the glass hook on the lower end of the stopper, B, making contact with glass and sulfuric acid only.

The autoclave, as shown in, F, in Fig. 1, and in detail

in Fig. 6, was 1 5/8 inches in diameter and 11 1/4 inches in length (inside measurements). A tight leak-proof closure was obtained by the use of an annealed copper gasket between the head and body.

Pyrex test tubes of 60 cc. capacity, with rubber stoppers were used as the reaction vessels for tests under atmospheric conditions.

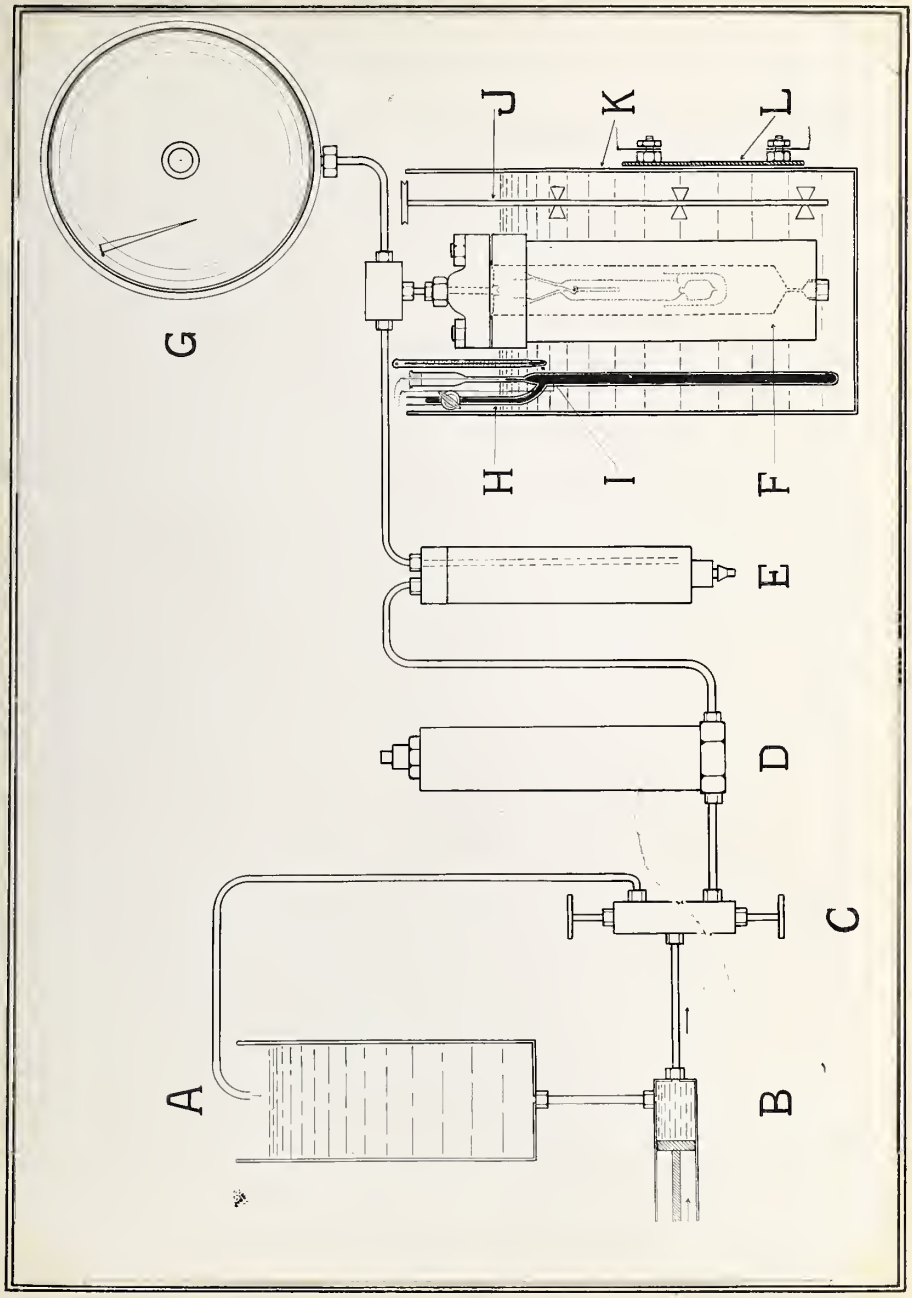
Analytical procedure

A sample of lead, of size and shape as already described, was thoroughly cleaned, washed in distilled water, and dried by a rinse in ethanol and ether. After letting the sample come to room temperature, it was weighed and then suspended on the hook at the end of the stopper, B, Fig. 2. The vessel, E, was filled with mercury to approximately the two-third level. Following this, the acid chamber, C, was filled, with a previously weighed quantity of acid, until all of the air was excluded when the stopper with the suspended metal was fitted into place. The exclusion of air was readily accomplished by adjusting the height of mercury in, E. The stopper was weighted with mercury to keep it in place, and finally the ground joint between the reaction chamber and the stopper was sealed with mercury. The whole was attached by means of a wire to the head of the autoclave, F, Fig. 1, which was then lowered into place

FIGURE 1

A .....Oil reservoir
B .....Hydraulic system
C ..... Two-way check valve
D ..... Relief valve
E ..... Surge tank
F ..... Autoclave
G ..... Bourdon-tube guage
H ..... Thermoregulator
I ..... Thermometer
J ..... Stirrer
K ..... Thermostat
L ..... Heater

FIGURE 1



and the autoclave filled to overflowing with oil. After seating the head, connection was made to the oil line and the pressure raised to the desired point by the operation of the hydraulic pump.

The metal was left under pressure for varying periods of time, the maximum being approximately four days. The lead was taken out for weighing after approximately 3, 9, 18, etc. hours in the acid. The exact intervening periods are shown in the respective tables.

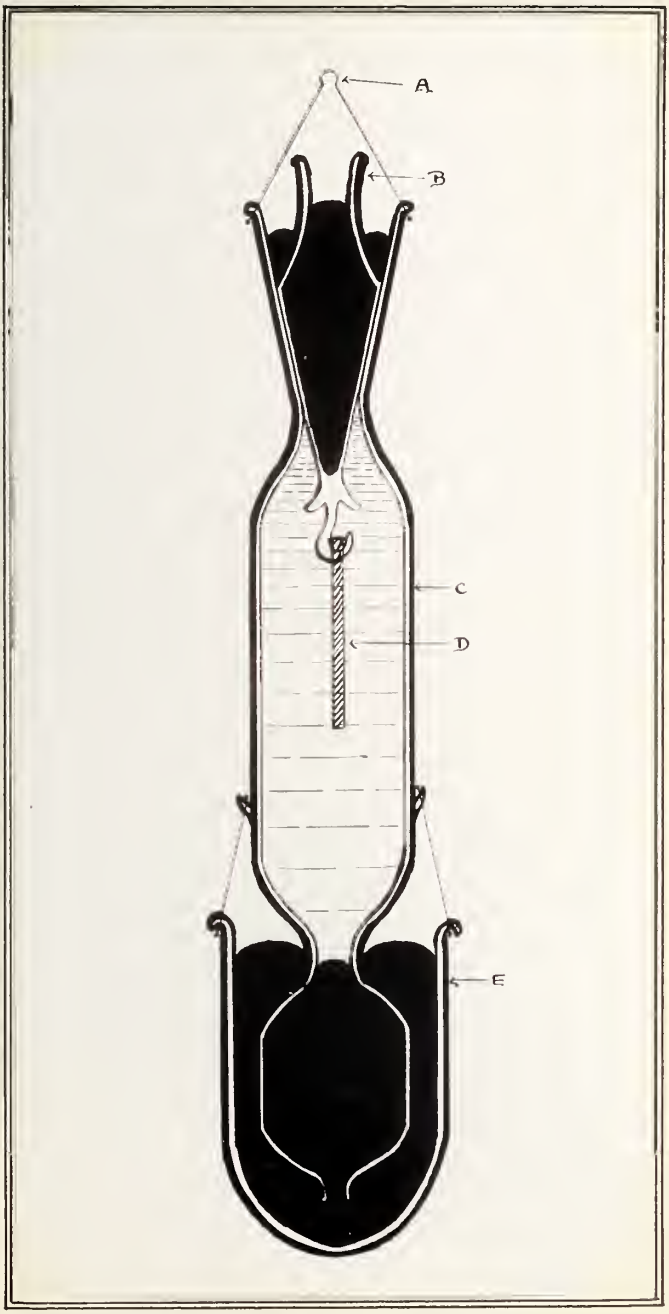
To remove the metal from the pressure system for weighing, the valve leading to the oil reservoir was partially opened, allowing the oil to run out until atmospheric pressure had been reached. The autoclave was opened, the reaction vessel detached, mercury seal removed by means of a capillary-tipped pipette, the stopper with the metal removed and washed in water, followed by alcohol and ether. After weighing it was immediately replaced according to the procedure already described for a further period of time.

In the controls under atmospheric pressure, a 60 cc. pyrex test tube was used. Thirty cc. of acid was poured into the vessel and the metal lowered, to rest on the bottom and against the wall as shown in Fig. 3. Cleaning, washing, drying and weighing of these samples followed the procedure described above.

FIGURE 2

A .... Wire for suspending
B .... Glass stopper with hook
C .... Reaction chamber
D .... The metal
E .... Mercury container

FIGURE 2



The various concentrations of acid were made up by diluting the 93% stock acid to the desired concentration. The specific gravity was read by means of a set of hydrometers. The major part of the work was carried out using the 93%, 77%, 62% and 37% concentrations. Less extensive experiments were carried out with solutions of 91%, 89% and 87% acid, 20% SO_3 fuming and 10% SO_3 fuming sulfuric acid.

The high pressure experiments were carried out at 1000 and 3,500 pound pressure per sq. inch, at 25°C., and at 3,500 pounds per sq. inch, at 40°C. The controls under atmospheric pressure were at room temperature (20-25 degrees C.), and at 40°C.

Results and Discussion

The experimental data is presented in the form of tables and as graphs. The tables are generally self-explanatory. The "Weight of Sample" at zero hours is the initial weight before placing in the acid. The following weights correspond to weights after the various times, measured from zero, tabled. The "Change in Weight" gives the total change in weight referred to the "Weight of the Sample" at zero hours time. The graphs are plots of the "Time" column plotted against the "Change in Weight" column.

One of the most noticeable features, based on observation, is the color change of the surface of the metal. The color passed through a series of purples, blues, and finally reached the metallic grey, or grey of the lead sulfate. This color change varied with the time and concentration, and appeared to be due to increasing thickness of the product formed on the surface. On the whole, it was observed that the film of corrosion products adhered very tenaceously, particularly where the corrosion was slight. A striking instance to show the nature of the surface layer, when corrosion was rapid, was observed with the 10% fuming acid solution. The surface layer appeared like a loose, bulky shell or crust, readily peeling off from the metal in complete sections.

TABLE I

Lead in Sulfuric Acid

Temperature ..... Room Temp.
Pressure ..... Atmospheric
Amount of Acid used ..... 30 cc.

	Time	Wt. After	Change
Wt. of Sample 5.7267 gm.	3 hrs.	5.7290	0.0023
Acid Conc.....93% .	9	5.7264	-0.0003
	18	5.7248	-0.0019
	30	5.7230	-0.0037
	48	5.7184	-0.0083
	72	5.7154	-0.0113
	122	5.7112	-0.0155
	170	5.7065	-0.0202
	242	5.7030	-0.0237
	27 days	5.6783	-0.0484
	62	5.6076	-0.1191
	116	5.4555	-0.2712
Wt. of Sample 5.4225 gm.	3 hrs.	5.4238	0.0013
Acid Conc.....77% .	9	5.4239	0.0014
	18	5.4238	0.0013
	30	5.4237	0.0012
	48	5.4237	0.0012
	72	5.4239	0.0014
	122	5.4239	0.0014
	170	5.4239	0.0014
	242	5.4239	0.0014
	27 days	5.4239	0.0014
	62	5.4227	0.0002
	116	5.4181	-0.0044

(Continued on next page)

TABLE I (Cont'd.)

	Time	Wt. After	Change
Wt. of Sample 6.0867 gm.	3 hrs.	6.0873	0.0006
Acid Conc.....62% .	9	6.0873	0.0006
	18	6.0876	0.0009
	30	6.0873	0.0006
	48	6.0873	0.0006
	72	6.0875	0.0008
	122	6.0875	0.0008
	170	6.0875	0.0008
	242	6.0882	0.0015
	27 days	6.0886	0.0019
	62	6.0901	0.0034
	116	6.0877	0.0010
Wt. of Sample 5.8007 gm.	3 hrs.	5.8009	0.0002
Acid Conc.....37% .	9	5.8014	0.0007
	18	5.8016	0.0009
	30	5.8020	0.0013
	48	5.8023	0.0016
	72	5.8032	0.0025
	122	5.8046	0.0039
	170	5.8054	0.0047
	242	5.8055	0.0048
	27 days	5.8055	0.0048
	62	5.8055	0.0048
	116	5.8051	0.0044

- - - - - - -

TABLE I a.

Lead in Sulfuric Acid

Temperature ..... Room Temp.
Pressure ..... Atmospheric.
Amount of Acid used ..... 30 cc.

	Time	Wt. After	Change
Wt. of Sample 5.3294 gm.	3 hrs.	5.1042	-0.2252
Acid Conc.... 20% Fuming	9	4.8083	-0.5211
	18	4.4869	-0.8425
	30	4.1975	-1.1319
	72	3.6660	-1.6634
	122	3.2229	-2.1065
	188	2.5214	-2.8080
	242	2.2681	-3.0613
	18 days	1.3804	-3.9490
	21	1.1215	-4.2079
	26	0.7186	-4.6108
Wt. of Sample 5.2476 gm.	3 hrs.	4.9441	-0.3035
Acid Conc..½ of 20% Fuming	9	4.7173	-0.5303
½ of 93%	18	4.5883	-0.6593
	30	4.3766	-0.8710
	72	3.9605	-1.2871
	122	3.6681	-1.5795
	188	3.4641	-1.7835
	242	3.4040	-1.8436
	18 days	3.2670	-1.9806
	21	3.2223	-2.0253
	26	3.1580	-2.0896

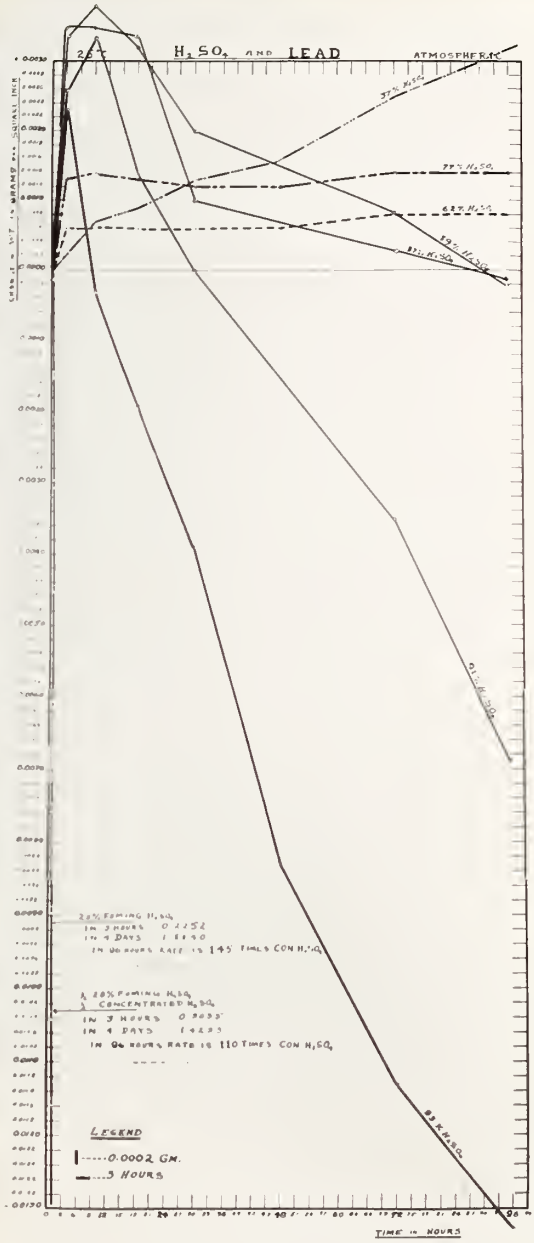
(Continued on next page.)

TABLE I a. (Cont'd.)

	Time	Wt. After	Change
Wt. of Sample 5.2704 gm.	3 hrs.	5.2730	0.0026
Acid Conc.....91% .	9	5.2738	0.0034
	18	5.2718	0.0014
	30	5.2704	0.0000
	72	5.2669	-0.0035
	122	5.2601	-0.0103
	188	5.2527	-0.0177
	242	5.2468	-0.0236
	18 days	5.2399	-0.0305
	21	5.2368	-0.0336
	26	5.2272	-0.0432
Wt. of Sample 5.3379 gm.	3 hrs.	5.3413	0.0034
Acid Conc.....89% .	9	5.3417	0.0038
	18	5.3411	0.0032
	30	5.3399	0.0020
	72	5.3387	0.0008
	122	5.3371	-0.0008
	188	5.3340	-0.0039
	242	5.3329	-0.0050
	18 days	5.3238	-0.0141
	21	5.3207	-0.0172
	26	5.3158	-0.0221
Wt. of Sample 5.1823 gm.	3 hrs.	5.1858	0.0035
Acid Conc.....87% .	9	5.1858	0.0035
	18	5.1857	0.0034
	30	5.1832	0.0009
	72	5.1826	0.0003
	122	5.1817	-0.0006
	188	5.1787	-0.0036
	242	5.1784	-0.0039
	18 days	5.1780	-0.0043
	21	5.1776	-0.0047
	26	5.1770	-0.0053

- - - - - - -

FIGURE 7


H_2SO_4 AND LEAD
ATMOSPHERIC
37% HCl
77% H_2SO_4
62% H_2SO_4
19% H_2SO_4
93% H_2SO_4
0.1% H_2SO_4
98% H_2SO_4
28% FUMING H_2SO_4
IN 3 HOURS 0.2252
IN 4 DAYS 1.8490
IN 96 HOURS RATE IS 145 TIMES CON H_2SO_4
80% FUMING H_2SO_4
& CONCENTRATED H_2SO_4
IN 3 HOURS 0.3035
IN 4 DAYS 1.6233
IN 96 HOURS RATE IS 110 TIMES CON H_2SO_4
LEGEND
0.0002 GM.
3 HOURS
TIME IN HOURS

Observation under conditions of room temperature and atmospheric pressure continued over relatively long periods of time - the longest being approximately four months. From these observations (shown graphically for the first four days only), it was evident that a film of lead sulfate first forms and this film either adheres to the metal, rendering it passive to further action by the sulfuric acid, or is dissolved by the acid, or does not adhere and offers little protection to the metal. The results obtained suggest that concentrations below 77% render the metal passive. There does not appear to be any definite concentration dividing the region of corrosion from the region of no corrosion as far as is known to the writer. It seems logical to assume that factors such as purity of the acid, metal, and conditions of temperature and so on, would make it impossible to do more than generalize on the approximate concentration where passivity would be permanent. It will be noted from Table 1, that for a one hundred and sixteen day period the lead in the 62% and 37% concentrations showed slight increase in weight, while in the 77% the change in weight, at first positive, crossed the "zero" line (original weight) after a period of two months and became negative. In the concentrations above 77% the rate of corrosion increases with concentration. The rate in the high concentrations is nearly a straight line function depending

TABLE II

Lead in Sulfuric Acid

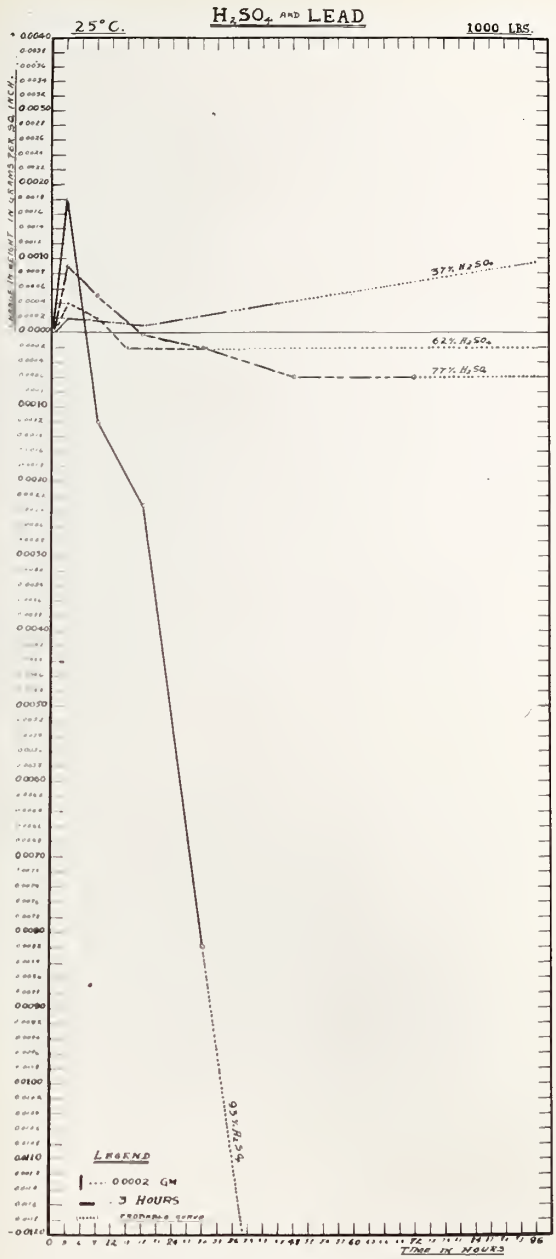
Temperature ..... 25 degrees C.
Pressure ..... 1000 pounds.

Acid Concentrations	93%	77%	62%	37%
Weight of Acid in gm.	47.7348	47.9970	41.1209	32.6979

	Time	Wt. After	Change
Wt. of Sample 5.6322 gm.	3 hrs.	5.6340	0.0018
Acid Conc.....93% .	9	5.6310	-0.0012
	18	5.6299	-0.0023
	30	5.6240	-0.0082
Wt. of Sample 5.5948 gm.	3 hrs.	5.5957	0.0009
Acid Conc.....77% .	9	5.5953	0.0005
	18	5.5948	0.0000
	30	5.5946	-0.0002
	48	5.5942	-0.0006
	72	5.5942	-0.0006
Wt. of Sample 5.4089 gm.	3 hrs.	5.4093	0.0004
Acid Conc.....62% .	9	5.4091	0.0002
	15	5.4091	0.0002
	27	5.4091	0.0002
Wt. of Sample 5.6727 gm.	6 hrs.	5.6729	0.0002
Acid Conc.....37% .	18	5.6728	0.0001
	43	5.6731	0.0004
	45	5.6731	0.0004

- - - - - - -

FIGURE 8


25°C.
H_2SO_4 AND LEAD
1000 LBS.
CHANGE IN WEIGHT IN GRAMS PER SQ. INCH
37% H_2SO_4
62% H_2SO_4
77% H_2SO_4
93% H_2SO_4
LEGEND
.0002 GM
3 HOURS
PROBABLE CURVE
TIME IN HOURS

on time and the amount of acid used - the lead would be completely converted to the sulfate in time, provided the acid did not fall below a certain concentration. It is obvious that if the quantity of metal available for corrosion was relatively l rge in comparison to the acid used, dilution would occur as the reaction proceeded until a passive state was reached due to the change in concentration.

It is interesting to note the relative rate of corrosion in 20% fuming sulfuric acid, 10% fuming sulfuric acid, and 93% sulfuric acid. Tables 1 and 1(a), and Figures 7 and 17 show, that over the first four days the rate of corrosion in the 20% fuming sulfuric acid was one hundred and forty-five times as rapid as in the concentrated acid alone, the rate decreasing to ninety times that in the 93% concentration at the end of twenty-six days. In the 10% fuming sulfuric acid, the rate was one hundred and ten times as fast over the first four days, in comparison to the 93% sulfuric acid rate, dimishing to forty times at the end of twenty-six days. This observed change in rate may be accounted for by the dilution of the acid which would take place with corrosion, by the decreased area of metal surface, and by the fact that the lead sulfate which precipitated out gathered around the metal at the bottom of the reaction vessel. A more satisfactory method would have been to

TABLE III

Lead in Sulfuric Acid

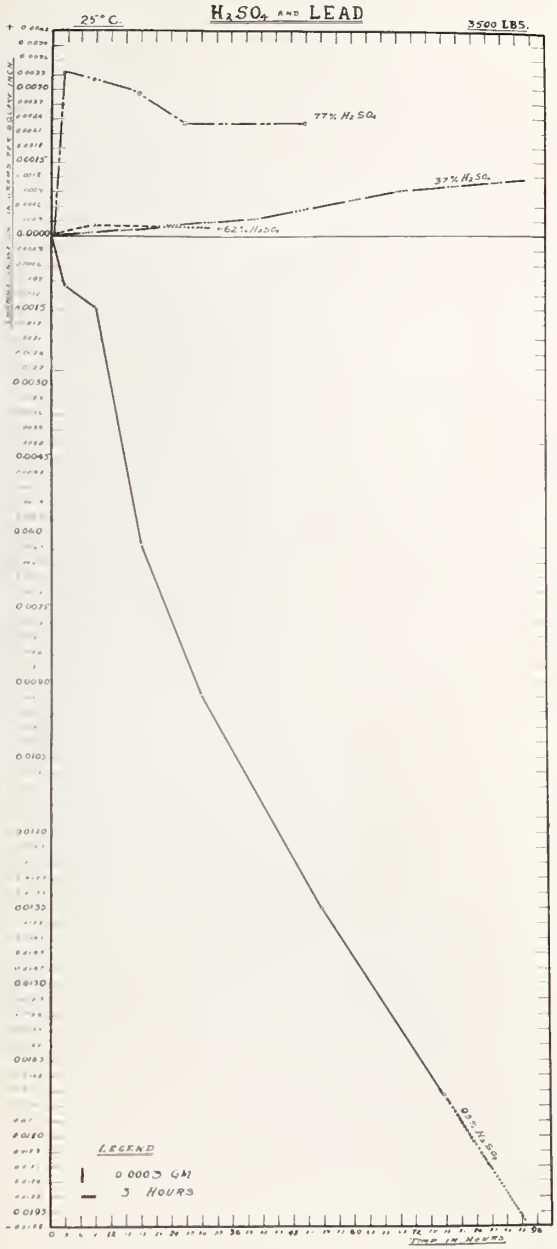
Temperature ..... 25 degrees C.
Pressure ..... 3500 pounds.

Acid Concentrations	93%	77%	62%	37%
Weight of Acid in gm.	47.4364	45.7817	41.1209	32.6979

	Time	Wt. After	Change
Wt. of Sample 5.7561 gm.	3 hrs.	5.7551	-0.0010
Acid Conc.....93% .	9	5.7547	-0.0014
	18	5.7499	-0.0062
	30	5.7470	-0.0091
	54	5.7426	-0.0135
	78	5.7386	-0.0175
	92.5	5.7348	-0.0213
Wt. of Sample 5.6374 gm.	3 hrs.	5.6408	0.0034
Acid Conc.....77% .	9	5.6406	0.0032
	18	5.6403	0.0029
	27	5.6397	0.0023
	51	5.6397	0.0023
Wt. of Sample 5.5812 gm.	3 hrs.	5.5813	0.0001
Acid Conc.....62% .	9	5.5814	0.0002
	22	5.5814	0.0002
Wt. of Sample 5.5336 gm.	3 hrs.	5.5336	0.0000
Acid Conc.....37% .	9	5.5337	0.0001
	21	5.5338	0.0002
	45	5.5340	0.0004
	69	5.5345	0.0009
	93	5.5347	0.0011

- - - - - - -

FIGURE 9


25° C.
H_2SO_4 AND LEAD
3500 LBS.
77% H_2SO_4
37% H_2SO_4
62% H_2SO_4
0.0000
0.0015
0.0030
0.0045
0.0060
0.0075
0.0090
0.0105
0.0120
0.0135
0.0150
0.0165
0.0180
0.0195
LEGEND
0.0003 GM
3 HOURS
TIME IN HOURS

suspend the metal in the acid in manner similar to that used in the pressure experiments.

A noticeable fact was the slow reaction in the 37% concentration. There is a gradual increase in weight in nearly every case observed whether under atmospheric or much higher pressure. The data of Tables, 1, 11, 111, 1V, and V, and Figures 7, 8, 9, 10 and 11, show this clearly. Two factors in corrosion may enter at this and similar concentrations. They are, first - ionization of the acid; and, second - the low solubility of lead sulfate in the dilute sulfuric acid. It appears that in such solutions, the lead sulfate is only slowly formed because of the impervious nature of the initial layer. Dilution of the acid results in a greater degree of ionization. Assuming that the sulfuric acid is the solvent, the increasing degree of ionization reduces the available sulfuric acid and consequently the solubility of the lead sulfate.

Comparing the results at two different temperatures, namely 25°C. and 40°C., under atmospheric conditions as shown in Tables 1, 1(a) and V, and Figures 7 and 11, it was surprising to find that the rate of corrosion in the 93% sulfuric acid was doubled by a fifteen degree rise, while the rate of corrosion in the 77%, 62% and 37% acids was practically unaffected. It may be suggested that the solubility of lead sulfate in 93%

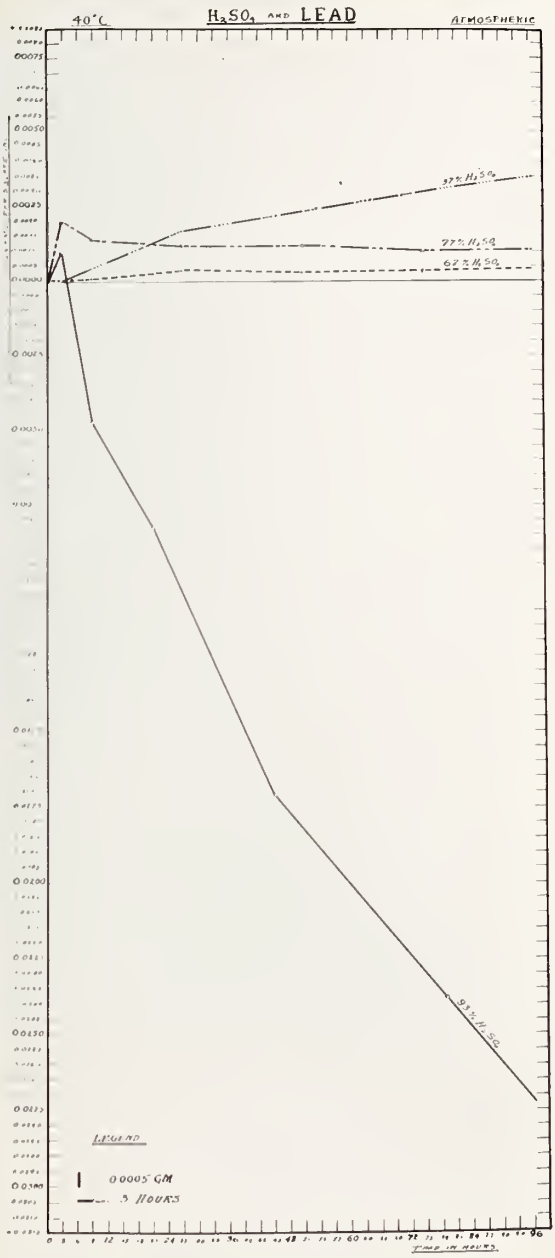
TABLE IV

Lead in Sulfuric Acid

Tempature ..... 40°C.
Pressure ..... Atmospheric.
Amount of Acid used ..... 30 cc.

	Time	Wt. After	Change
Wt. of Sample 5.7291 gm.	3 hrs.	5.7301	0.0010
Acid Conc.....93% .	9	5.7244	-0.0047
	21	5.7209	-0.0082
	45	5.7120	-0.0171
	79	5.7053	-0.0238
	6 days	5.7000	-0.0291
	15	5.6761	-0.0530
Wt. of Sample 5.5165 gm.	3 hrs.	5.5185	0.0020
Acid Conc.....77% .	9	5.5179	0.0014
	27	5.5177	0.0012
	51	5.5177	0.0012
	75	5.5175	0.0010
	99	5.5176	0.0011
	11 days	5.5170	0.0005
Wt. of Sample 5.6856 gm.	3 hrs.	5.6856	0.0000
Acid Conc.....62% .	9	5.6857	0.0001
	21	5.6860	0.0004
	45	5.6859	0.0003
	99	5.6860	0.0004
	6 days	5.6860	0.0004
Wt. of Sample 5.6562 gm.	3	5.6562	0.0000
Acid Conc.....37% .	21	5.6579	0.0017
	69	5.6593	0.0031

FIGURE 10


40°C
H_2SO_4 AND LEAD
ATMOSPHERIC
97% H_2SO_4
77% H_2SO_4
62% H_2SO_4
93% H_2SO_4
LEGEND
0.0005 GM
3 HOURS
TIME IN HOURS

acid increases rapidly with increased temperature, or the porosity of the deposit increases with temperature permitting more rapid attack of the metallic lead. On the other hand, the solubility of lead sulfate in dilute acid is not greatly affected by temperature, or more likely, the porosity of the deposit is unaffected by a rise in temperature. The general conclusion is that the passivity of lead in lower concentrations of acid, due to a coating of lead sulfate is nearly independent of changing temperature.

The effects of high pressure may be seen in the data of Tables II and III (25°C.) and Table V (40°C.) and more readily in Figures 8, 9 and 11. In 93% sulfuric acid at 1,000 pounds pressure per sq. inch, (Table II, Figure 8), the rate over the first thirty hours is double that found with the same acid under atmospheric pressure (Figure 17). In the other three concentrations there appears to be a greater solubility of the sulfate at the higher pressure, since the metals in both the 77% and 62% concentrations go below their original weight, while the increase in weight in the 37% acid is very much less. In 37% acid at the forty-five hour mark, the increase in weight at a pressure of 1,000 pounds per sq. inch is only one quarter of that found under atmospheric conditions.

When the pressure was raised to 3,500 pounds per sq.

TABLE V

Lead in Sulfuric Acid

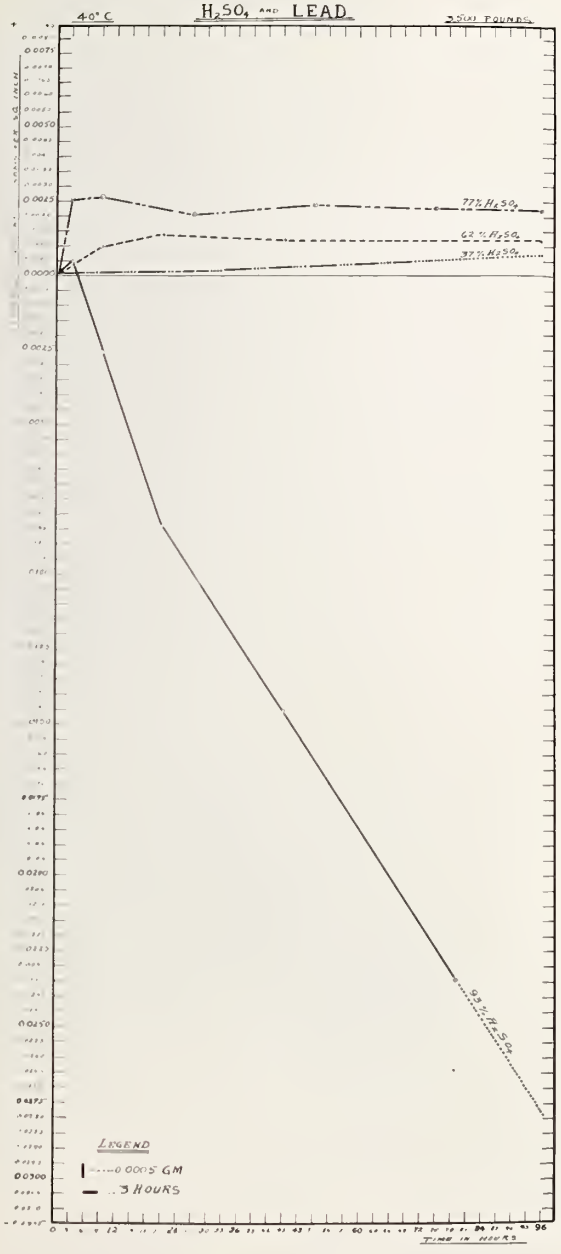
Temperature ..... 40 degrees C.
Pressure ..... 3,500 pounds.

Acid Concentrations	93%	77%	62%	37%
Weight of Acid in gm.	47.4999	46.0468	48.4339	32.3561

	Time	Wt. After	Change
Wt. of Sample 5.4428 gm.	3 hrs.	5.4433	0.0005
Acid Conc.....93% .	9	5.4403	-0.0025
	21	5.4345	-0.0083
	45	5.4283	-0.0145
	79	5.4194	-0.0234
Wt. of Sample 5.6984 gm.	3 hrs.	5.7010	0.0026
Acid Conc.....77% .	9	5.7011	0.0027
	27	5.7005	0.0021
	51	5.7008	0.0024
	75	5.7007	0.0023
	99	5.7006	0.0022
Wt. of Sample 5.7416 gm.	3 hrs.	5.7420	0.0004
Acid Conc.....62% .	9	5.7426	0.0010
	21	5.7430	0.0014
	45	5.7428	0.0012
	99	5.7428	0.0012
Wt. of Sample 5.5347 gm.	3 hrs.	5.5347	0.0000
Acid Conc.....37% .	21	5.5348	0.0001
	69	5.5352	0.0005

- - - - - - -

FIGURE 11


40° C
H_2SO_4 AND LEAD
3.501 POUNDS
77% H_2SO_4
62% H_2SO_4
37% H_2SO_4
93½% H_2SO_4
LEGEND
0.0005 GM
3 HOURS
TIME IN HOURS

inch as shown in Tables III and V, and Figures 9 and 11, the rate of corrosion in the 93% acid shows only a slight increase as compared to the rate at 1,000 pounds pressure (Figure 17), at the end of thirty hours, and ends up with an approximate increase of 50% over the atmospheric pressure rate at the end of four days (Figure 17). From Figures 7, 8, 9 and 11, it will also be noticed that in the 77% acid the increase in the weight of metal indicates that the amount of sulfate adhering to the metal is nearly three times that found under atmospheric conditions. The 62% and 37% concentrations behave in a manner almost identical to that under atmospheric conditions.

Summarizing, it may be said that the rate of corrosion in 93% sulfuric acid increases markedly with increasing temperature at atmospheric pressure. At high pressures the effect of temperature appears to be negligible. No explanation can be offered for this contrasting behaviour, but it may be suggested that the structure of the lead sulfate alters under high pressures in such a way as to eliminate any temperature effect. In the dilute solutions, the slight, or negligible effect of temperature under all conditions of pressure suggests that the nature of the lead sulfate film is independent of pressure.

Several points of interest were noted with respect to the cases of more rapid and extensive corrosion, as with

fuming sulfuric acid.

Macroscopic and microscopic examination showed that corrosion was intercrystalline and along slip planes of individual crystals, as might be expected.

Further interesting observations were made on the color change in fuming sulfuric acid solutions after different periods of reaction with the metal. In the 20% fuming sulfuric acid an ultramarine blue color appeared in the solution, adjacent to the metal, in approximately fifteen minutes, while in the 10% fuming sulfuric acid yellow-greens and green-blues appeared with the blue color farthest away from the metal and the yellow immediately next to the metal. After several weeks the ultramarine blue solution gradually changed and assumed a chocolate-brown appearance.

To arrive at the cause of the formation of the color, observations were carried out using a number of lead salts, arsenic salts, arsenic metal, zinc, copper, antimony, tellurium, selenium, and lead shot containing arsenic. Similar color changes appeared with arsenic metal, which on long standing changed over to the same chocolate-brown as observed with lead. Antimony produced a brown; most of the salts a brown; zinc showed only a minute amount of blue next to the metal; copper a slightly different shade of blue; while tellurium and selenium produced

their well known colors of red and green. This suggested that impurities such as arsenic in particular, might be a source of the color changes, but the slow rate of color formation with these substances suggested the possibility of another cause - such as a product of the reaction between lead and acid. The only possibility was sulfur, a product of the reduction of the acid by metal. On making analagous tests with sulfur the colors appeared like those already observed, but the rate of color formation was much faster. Since sulfur was also formed with the other metals it is suggested that sulfur was the source of the colors in both cases. The phenomena of color changes observed here have been observed elsewhere in work on the liberation of sulfur in the same and different solutions according to Mellor (11).

Further examination of the colors produced with metals in the fuming sulfuric acids, and with sulfur in similar solutions showed that the greens were produced either on dilution of the fuming sulfuric acid or after long standing which resulted in the deposition of increased amounts of sulfur. In solutions approaching the 100% sulfuric acid the sulfur tends to produce a yellow coloration instead of greens and blues. After long periods the fuming acid solution (reacting with the metal) produced chocolate-browns. This was especially noticeable near the surface of the solution where water from the air

could be absorbed. A similar condition was obtained by dropping a piece of sulfur into the 20% fuming sulfuric acid. The solution immediately next to the sulfur became blue, later changing over to brown. This was also the case with a bit of porous non-crystallized sulfur floating at the surface of the fuming sulfuric acid solution. In the 10% fuming acid a yellow cloud-like formation appeared next to the metal, which merged slowly into greens and the greens merged into blues - suggesting dispersion of the sulfur molecules through the liquid.

As a result of these observations the following conclusion has been reached: the metal reduces the fuming sulfuric acid and free colloidal sulfur is formed. Initially, when finely dispersed, these solutions are blue. With changing degree of dispersion, presumably by growth in size of the sulfur particles, the color changes through the sequence of colors to brown. It is probable that pyrosulfuric acid is the compound reduced and that the colloidal sulfur consists largely of thionic acids or similar complex bodies. Oden's sulfur sol has been shown by Freundlich and Scholz (4) to be a combination of sulfur and pentathionic acid, $H_2S_5O_6$, and is formed by the reduction of sulfur compounds.

Observations seem to favor the colloidal interpretation, since on pouring some of the blue solution into distilled water, an opalescent solution resulted which cleared on adding sodium

chloride; similarily on adding sodium chloride to the colored fuming sulfuric acid, it decolorized completely, passing through various shades of brown to light amber. This behaviour is typical of the behaviour of colloidal sulfur solutions.

Summary and Conclusions

High pressures at 25°C. show a definite increase in the rate of corrosion of lead in sulfuric acid, with the 93% concentration showing the effect to the greatest extent.

Increasing pressure has little or no effect on the rate of corrosion of lead in the 93% sulfuric acid at 40°C., but does show some differences in the lower concentrations and at 25°C.

The accepted belief that solubility of lead sulfate increases with increased acid concentration is consistent with the results observed.

Reduction to free sulfur occurs at least in the 93% concentration and upwards, and colloidal solutions of sulfur are formed in the fuming acids giving rise to various colored solutions. (For sulfur analysis of the precipitates formed see General Discussion at the end of Part III.)

PART II.

The Action of Sulfur Dioxide and Hydrogen Sulfide on Lead Immersed in Sulfuric Acid.

PLATE 3

Showing part of the analytical lab.: From left to right - Kipp generator for SO_2, and reaction vessels; modified Referee's apparatus for sulfur analysis; the reaction vessels for hydrogen sulfide and natural gas determinations under atmospheric pressure.

PART II

Introduction

Before proceeding to examine the action occuring with sulfuric acid gas scrubbers, it was considered of interest to carry out observations on actions resulting when sulfur dioxide and hydrogen sulfide were passed through sulfuric acid containing a lead sample. Lack of time and equipment did not permit this work to be carried out under pressure, but it was considered that a certain amount of definite information could be obtained by observing the rate of corrosion under atmospheric pressure. The sulfur compounds in odorized Viking gas include mercaptans which have some properties in common with hydrogen sulfide. This, together with presence of sulfur dioxide in the off-gases from the scrubbers, make this part of the investigation of interest.

It was expected, and found, that the corrosion of lead under the above conditions when compared with the findings of Part 1, would permit of some conclusions as to the origin of the corrosion in the scrubbers.

Although it has not been taken into account, it should be pointed out that the agitation of the solutions by the passage of the gases might have had an accelerating influence on the rate of corrosion, as compared to the results obtained in Part 1.

Literature Review

The literature on this phase of corrosion is not very extensive. There is sufficient to indicate that the rate of corrosion of lead in mixed sulfuric acid and sulfurous acid solutions is greater than in sulfuric acid solutions alone. This suggests that lead sulfite is either more soluble than lead sulfate or is less adherent to the metal. Another explanation is offered later, on the data of this work. No data is available in the literature on either point. It is probable that sulfur dioxide will react with water even in the presence of sulfuric acid to give sulfurous acid as follows:

$$SO_2 + H_2O = H_2SO_3 \qquad (1)$$

Should the sulfurous acid attack the lead, it is almost certain that the resulting lead sulfite will be decomposed by sulfuric acid regenerating sulfurous acid and depositing lead sulfate:

$$H_2SO_3 + Pb = PbSO_3 + H_2 \qquad (2)$$

$$H_2SO_4 + PbSO_3 = PbSO_4 + H_2SO_3 \qquad (3)$$

As an alternative reaction, suggested chiefly to account for the formation of free sulfur, the oxidation of sulfurous acid by sulfur dioxide is offered:

$$2H_2SO_3 + SO_2 = 2H_2SO_4 + S \qquad (4)$$

$$2PbSO_3 + SO_2 = 2PbSO_4 + S \qquad (5)$$

No evidence exists, to the author's knowledge, confirming these reactions. It is well known, however, that sulfurous

acid solutions are unstable and may change slowly to sulfuric acid with a deposition of sulfur. Ostwald (13) states that heating the solution results in deposition of sulfur with formation of sulfuric acid. Exposure to light gives the same result. It is suggested that the reaction (4) above offers a reasonable explanation. The sulfurous acid may be considered as a reducing agent and sulfur dioxide as an oxidizing agent.

In the case of the reaction with hydrogen sulfide, the primary reaction may be taken as follows, with little doubt:

$$H_2S + H_2SO_4 = S + H_2O + SO_2 \qquad (6)$$

In the presence of sulfur dioxide, hydrogen sulfide undergoes the following reaction:

$$2H_2S + SO_2 = 2H_2O + 3S \qquad (7)$$

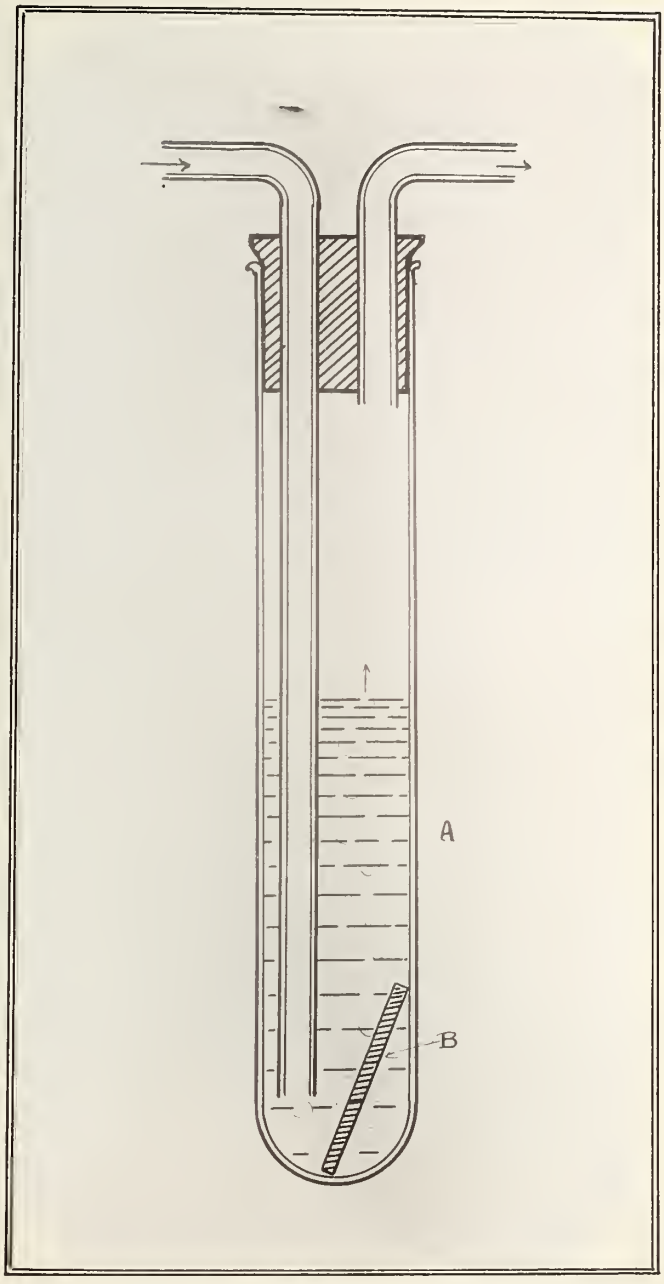
Finally, sulfur dioxide reacting with water yields sulfurous acid as in equation (1) above. Corrosion would then proceed according to the same mechanism assumed for solutions of sulfur dioxide in sulfuric acid. The completeness of reactions as shown in equations (6) and (7) above, eliminates any corrosive action due to hydrogen sulfide itself by its prompt decomposition to sulfur and sulfur dioxide.

FIGURE 3

A .... 60 cc. pyrex test tube

B .... Metal in position

FIGURE 3



Experimental

Materials

The metal and sulfuric acid solutions were prepared in the manner already described in Part 1.

The sulfur dioxide was generated by the action of a very weak solution of sulfuric acid on C. P. sodium sulfite.

The hydrogen sulfide was prepared by the usual laboratory method - commercial hydrochloric acid on sticks of iron pyrites.

Apparatus

The reaction vessel was essentially as shown in Figure 3. It consisted of a 60 cc. pyrex test tube fitted with a rubber stopper carrying two glass tubes, one of which, for the introduction of the gas, dipped well below the surface of the acid.

Kipp gas generators were used for the production of sulfur dioxide and hydrogen sulfide.

The gases were dried by passage over anhydrous calcium chloride before passage through the acid solutions.

Analytical Procedure

(1) Sulfur Dioxide Experiments: The kipp generator was connected to a U-tube containing calcium chloride, which in turn was connected to a series of five reaction vessels. The

sulfur dioxide passed through the series of solutions in the following order: Through the 93%, then through the 77%, 62%, 37%, and finally distilled water, in the order named. Connecting the vessels in series was considered satisfactory since the pressure generated was sufficient to bubble the gas slowly through the entire series of solutions and keep them saturated. An absorption tower filled with soda-lime at the end of the train took care of the excess sulfur dioxide.

(2) Hydrogen Sulfide Apparatus: In this series two different sets of connections were used. The first set was carried out using connections in series, as for the sulfur dioxide experiment. This was not found satisfactory since the hydrogen sulfide was all decomposed in the first or 93% acid solution, unless suction was used to draw the gas through very rapidly. The more satisfactory method was to connect the five reaction vessels in parallel. This was accomplished by passing the hydrogen sulfide through a manifold chamber to which was fitted a five-hole stopper carrying five short glass tubes. Rubber tubes led from this distributing system to each of the reaction vessels. Each rubber tube was fitted with a screw clamp by means of which the gas flow to each reaction vessel could be regulated, or shut off when the sample was removed for weighing.

Weighings were carried out after suitable periods of

time. These periods were chosen with two purposes in mind: (1) To give periods comparative to those in Part 1; (2) To give some comparative periods of time regarding the particular metal and solution itself.

Results and Discussion

Discussion on the Effect of Sulfur Dioxide

From observations presented in Part 1, it was concluded that the rate of corrosion depended largely on the concentration of the sulfuric acid. Apart from any action of sulfurous acid itself, it might be expected that the saturation of the solution with sulfur dioxide would increase the rate of corrosion due to a virtual increase in sulfuric acid concentration brought about by the removal of water as sulfurous acid. The reaction (4), if admitted, would also result in an increase in sulfuric acid concentration. While reaction (3) results in the loss of sulfuric acid, it does not involve water and would not alter the water content. However, should reaction (3) predominate, corrosion would have to be assigned to sulfurous acid.

From the observations based on reactions for a period of eighty-four days, the rate of corrosion in the 93% sulfuric acid which was saturated with sulfur dioxide was nearly thirteen times as rapid as in the 93% acid alone. These data are shown

in Tables I and VI, and graphically in Figures 7, 12 and 17. This would indicate at first sight, that sulfur dioxide or sulfurous acid is definitely a corrosive agent. However, in Part I, it was shown that the corrosive action of sulfuric acid increases rapidly with concentration above 90%. As shown in Figure 7, and Tables 1 and 1 (a), the rate of corrosion increases by a factor of three for the 2% increase in concentration between 91% and 93%. The removal of water by reaction (1) from 93% acid to the extent of 7% could easily account for the factor of 13, as shown in Tables 1 and VI, and Figure 12, for the first four days.

In the 77% concentration (Table VI, Figure 12), it may be observed that an increase in weight takes place for about the first three days. Sometime after this, rapid corrosion commenced, similar in magnitude to that in the 93% acid alone, and lasted until the tenth day. At this time the corrosion almost ceased or became passive for a considerable time. However, between the twenty-seventh and sixty-second days slight corrosion occurred, but increased rapidly between the sixty-second and the final reading on the eighty-fourth day. The rate between the readings on the sixty-second and eighty-fourth days was five times that in 93% sulfuric acid alone. However, it is certain that the rate was much greater, probably increasing regularly from a small value at the sixty-second day to a large value (much more than five times as great) as that found with the

TABLE VI

Lead in Sulfuric Acid Sat. with Sulfur Dioxide

Temperature ..... Room Temp.
Pressure ..... Atmospheric.

	Time	Wt. After	Change
Wt. of Sample 5.6915 gm.	3 hrs.	5.6909	-0.0006
Acid Conc.....93% .	9	5.6914	-0.0001
	27	5.6492	-0.0423
	51	5.6012	-0.0903
	75	5.5521	-0.1394
	7 days	5.4063	-0.2852
	10	5.3113	-0.3802
	14	5.2098	-0.4817
	27	4.8545	-0.8370
	62	4.1337	-1.5578
	84	3.4578	-2.2337
Wt. of Sample 5.4837 gm.	3 hrs.	5.4836	-0.0001
Acid Conc.....77% .	9	5.4837	0.0000
	27	5.4839	0.0002
	51	5.4839	0.0002
	75	5.4843	0.0006
	7 days	5.4662	-0.0175
	10	5.4577	-0.0260
	14	5.4576	-0.0261
	27	5.4558	-0.0279
	62	5.4507	-0.0330
	84	5.1272	-0.3565

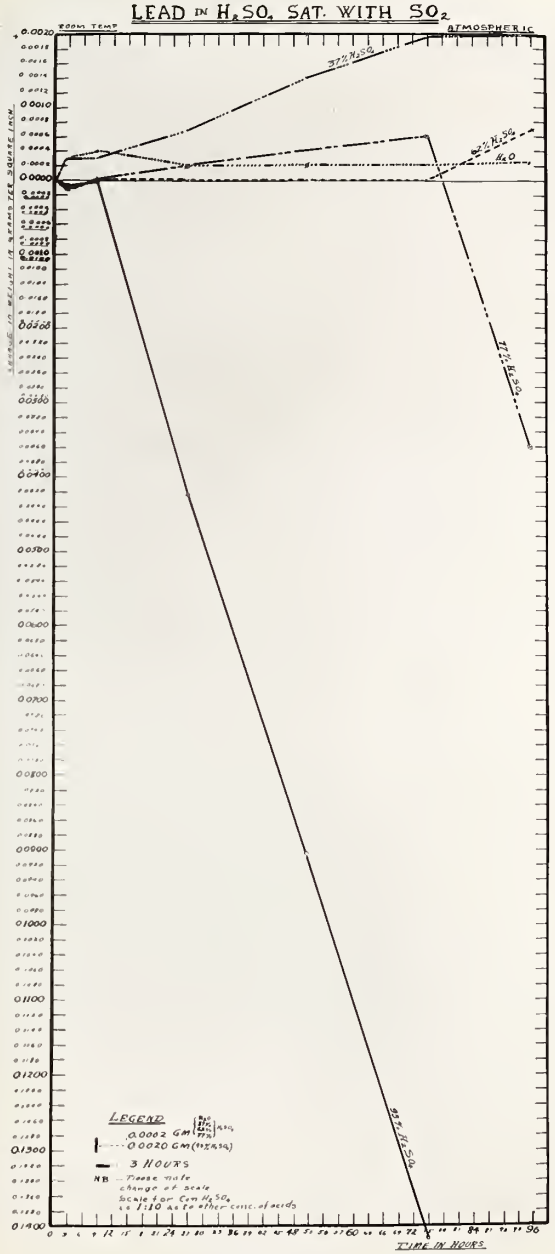
(Continued on next page.)

TABLE VI (Cont'd.)

	Time	Wt. After	Change
Wt. of Sample 5.4229 gm.	3 hrs.	5.4228	-0.0001
Acid Conc.....62% .	9	5.4229	0.0000
	27	5.4229	0.0000
	51	5.4229	0.0000
	75	5.4229	0.0000
	7 days	5.4260	0.0031
	10	5.4279	0.0050
	14	5.4286	0.0057
	27	5.4286	0.0057
	62	5.4223	-0.0006
	84	5.4200	-0.0029
Wt. of Sample 5.6508 gm.	3 hrs.	5.6511	0.0003
Acid Conc.....37% .	9	5.6511	0.0003
	27	5.6515	0.0007
	51	5.6522	0.0014
	75	5.6528	0.0020
	7 days	5.6534	0.0026
	10	5.6540	0.0032
	14	5.6546	0.0038
	27	5.6562	0.0054
	62	5.6483	-0.0025
	84	5.6448	-0.0060
Wt. of Sample 5.8247 gm.	3 hrs.	5.8250	0.0003
Water & Sulfur Dioxide	9	5.8251	0.0004
	27	5.8249	0.0002
	51	5.8249	0.0002
	75	5.8249	0.0002
	7 days	5.8251	0.0004
	10	5.8251	0.0004
	14	5.8253	0.0006
	27	5.8257	0.0010
	62	5.8287	0.0040
	84	5.8344	0.0097

- - - - - - -

FIGURE 12


LEAD IN H_2SO_4 SAT. WITH SO_2
ROOM TEMP
ATMOSPHERIC
37% H_2SO_4
87½ H_2SO_4
H_2O
11% H_2SO_4
97½ H_2SO_4
LEGEND
0.0002 Gm
0.0020 Gm
3 HOURS
TIME IN HOURS

93% acid, at the eighty-fourth day.

Little can be said as to the cause of such phenomena. If one is permitted to speculate, there are three and possibly four distinct parts to the curve. The first part, covering three days, may be considered due to the formation of lead sulfate on the metal surface, while sulfur dioxide is saturating the solution and removing water as sulfurous acid. After three days time, the water content is so low that corrosion can occur. The reaction continues with the formation of the lead sulfate and and lead sulfite until the solution is saturated at about the tenth day. Thereafter one can assume the slow conversion of sulfurous acid by reaction (4) to sulfuric acid. As the sulfuric acid concentration increases, the rate of corrosion increases due to increased solubility of the lead sulfate. This steadily increasing rate will go on to a maximum between the sixty-second and eighty-fourth day when the liquid is pure sulfuric acid containing sulfur dioxide but no sulfurous acid in solution.

The corrosion of lead in pure water containing sulfur dioxide and sulfurous acid, as shown in Table VI and Figure 12, was slight. This indicates that sulfurous acid is not a satisfactory solvent for lead sulfite, possibly lead sulfate also, should oxidation have occured. Lead sulfite, according to data reviewed by Mellor (12) is not soluble in water but is soluble

TABLE VII

Lead in Sulfuric Acid with Hydrogen Sulfide Gas.

Temperature ..... Room Temp.
Pressure ..... Atmospheric.
Amount of Acid used ..... 30 cc.

The Hydrogen Sulfide was passed through the five solutions with the test tubes connected in parallel - equalized volume control was made possible by the use of screw clamps.

	Time	Wt. After	Change
Wt. of Sample 5.3241 gm.	9 hrs.	5.3169	-0.0072
Acid Conc.....93% .	18	5.3212	-0.0029
	27	5.2714	-0.0527
	51	5.2589	-0.0652
	75	5.2507	-0.0734
	7 days	5.2321	-0.0920
Wt. of Sample 5.3599 gm.	9 hrs.	5.3692	0.0093
Acid Conc.....77% .	18	5.3611	0.0012
	27	5.3593	-0.0006
	51	5.3595	-0.0004
	75	5.3589	-0.0010
	7 days	5.3549	-0.0050
Wt. of Sample 5.3116 gm.	9 hrs.	5.3115	-0.0001
Acid Conc.....62% .	18	5.3116	0.0000
	27	5.3115	-0.0001
	51	5.3116	0.0000
	75	5.3125	0.0009
	7 days	5.3154	0.0038

(Continued on next page.)

TABLE VII (Cont'd)

	Time	Wt. After	Change
Wt. of Sample 5.3391 gm.	9 hrs.	5.3392	0.0001
Acid Conc.....37% .	18	5.3393	0.0002
	27	5.3394	0.0003
	51	5.3396	0.0005
	75	5.3401	0.0010
	7 days	5.3416	0.0025
Wt. of Sample 5.3889 gm.	9 hrs.	5.3884	-0.0005
Water	18	5.3884	-0.0005
	27	5.3884	-0.0005
	51	5.3882	-0.0007
	75	5.3882	-0.0007
	7 days	5.3882	-0.0007
Wt. of Sample 5.3591 gm.	9 hrs.	5.3590	-0.0001
In dry H_2S	18	5.3590	-0.0001
	27	5.3587	-0.0004
	51	5.3584	-0.0007
	75	5.3584	-0.0007
	7 days	5.3583	-0.0008

- - - - - - -

FIGURE 13

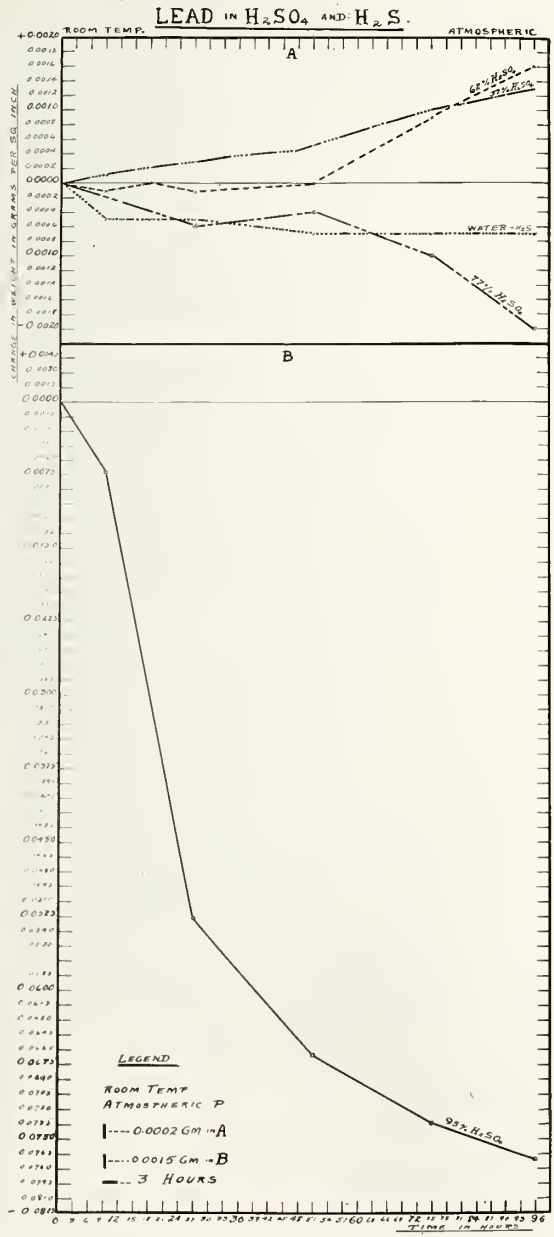

LEAD IN H_2SO_4 AND H_2S.
ROOM TEMP.
ATMOSPHERIC
A
B
62% H_2SO_4
77% H_2SO_4
WATER + H_2S
77% H_2SO_4
93% H_2SO_4
LEGEND
ROOM TEMP
ATMOSPHERIC P
0.0002 GM in A
0.0015 GM in B
3 HOURS
TIME IN HOURS

TABLE VIII

Lead in Sulfuric Acid with Hydrogen Sulfide Gas.

Temperature ..... Room Temp.
Pressure ..... Atmospheric.
Amount of Acid used ..... 30 cc.

The H_2S was passed through the five solutions with the test tubes connected in series, passing through the 93%, 77%, 62%, 37% acid solutions, and water, in the order named.

	Time	Wt. After	Change
Wt. of Sample 5.7705 gm.	9 hrs.	5.7537	-0.0168
Acid Conc.....93% .	21	5.7338	-0.0367
	45	5.6867	-0.0838
	75	5.6463	-0.1242
Wt. of Sample 5.6993 gm.	9 hrs.	5.6993	0.0000
Acid Conc.....77% .	21	5.6993	0.0000
	45	5.6993	0.0000
	75	5.6992	-0.0001
Wt. of Sample 5.5951 gm.	9 hrs.	5.5952	0.0001
Acid Conc.....62% .	21	5.5953	0.0002
	45	5.5954	0.0003
	75	5.5955	0.0004
Wt. of Sample 5.5909 gm.	9 hrs.	5.5909	0.0000
Acid Conc.....37% .	21	5.5912	0.0003
	45	5.5914	0.0005
	75	5.5922	0.0013
Wt. of Sample 5.7747 gm.	9 hrs.	5.7740	-0.0007
Water & Hydrogen Sulfide	21	5.7738	-0.0009
	45	5.7730	-0.0017
	75	5.7716	-0.0031

- - - - - - -

in acid solutions.

Discussion on the Effect of Hydrogen Sulfide

According to the generally accepted reactions (6) and (7), we may assume that sulfur dioxide and sulfur will be products of the reactions. Considerations of the rate of corrosion, where hydrogen sulfide was bubbled through the acid solutions, may be based on these reactions. It appeared that hydrogen sulfide was immediately decomposed in 93% sulfuric acid. The decomposition in the lower concentrations of acid was much slower, and appeared slight in the 62% concentration, with no visible precipitate of sulfur appearing in the 37% concentration.

Some of the sulfur evidently dissolved in acid producing a greenish to a bluish tint in the solution, but on saturation, or near saturation, precipitates out in the yellow form.

In the case of the 93% acid the large quantity of sulfur formed did not adhere very tenaceously to the metal. The sulfur separated quite readily when washed, leaving only a thin coat of sulfate adhering to the metal. The reverse was the case in the 77% concentration, the sulfur adhering to the metal so tenaceously that it was impossible to remove it completely without the use of hot organic solvents, like benzene or carbon bisulfide. The first few weighings as shown in Table VII are abnormal due to the

adhering sulfur. It is advisable to discount these figures and only accept the final readings - when the metal was thoroughly cleaned of the sulfur.

Table VII indicates clearly the results obtained, and from the composite graph (Figure 17) the fact may be observed that the rate of corrosion in the 93% solution saturated with hydrogen sulfide, is almost identical to that of the 93% concentration saturated with sulfur dioxide. Assuming the possibility of instantaneous conversion of hydrogen sulfide to sulfur dioxide in the concentrated solution, we would have conditions similar, if not identical, to those already discussed under sulfuric acid solutions which were saturated with sulfur dioxide. The results from other concentrations of acid with hydrogen sulfide are in fair agreement with the same concentrations and sulfur dioxide. The rate of decrease in the 77% solution is slower for the seven days under observation. This may be explained by the fact that the sulfur formed adhered exceedingly tenaceously, as already explained, exhibiting a reduced rate of corrosion due to decreased surface of the metal being exposed to corrosive action of the solution. The deposition of sulfur on the metal suggests a catalysed reaction on the surface.

Conclusions and Summary

The saturation of sulfuric acid solutions by passing sulfur dioxide or hydrogen sulfide through them, results in a very noticeable acceleration in the rate of corrosion - the rate being increased thirteen times in the 93% sulfuric acid.

The anomalous behaviour of the 77% acid with sulfur dioxide suggests that both the water content and sulfurous acid content play an important part in the process of corrosion.

The rate of corrosion of lead in sulfuric acid saturated with sulfur dioxide is nearly identical with that found using the same acids with hydrogen sulfide, suggesting a common basis.

It is suggested that the increased rate of corrosion in the presence of sulfur dioxide in the acid solutions, is due to the elimination of water as sulfurous acid with a resulting increased solubility of the sulfate and sulfite. Further it is suggested that sulfurous acid, after comparatively long periods of time, is completely oxidized, directly or indirectly to sulfuric acid - therefore the increased rate of solubility of the sulfate and corrosion.

Finally, the evidence is fairly clear that hydrogen sulfide is only an indirect method of adding sulfur dioxide to the solutions, since the results obtained were much the same with either gas.

PART III

The Corrosion of Lead by Sulfuric Acid in Desulfurizing Gas Pressure Scrubbers.

Introduction

As the final part of this work, the reproduction of conditions existing in sulfuric acid gas scrubbers was carried out in a manner permitting quantitative measurements of corrosion. In brief, a sample of lead was suspended in sulfuric acid through which a controlled stream of odorized Viking gas was passed. By observation of the rate of corrosion, and determination of the sulfur content of the gas, it was hoped to obtain data that could be correlated with the results of Part I and Part II. While acid concentrations other than 93% had no bearing on the purely local problem of the scrubber gases, the investigation was extended to include the lower concentrations - chiefly for purposes of correlation with the general problem.

Literature Review

Nothing has been reported in the literature on this particular problem. However, much information of value is available in the literature on the refining of petroleum by treatment with sulfuric acid, for the removal of sulfur compounds (6). This work is of importance since the odorants added to Viking natural gas consist essentially of vapors of liquid sulfur compounds recovered in the process of refining sulfur bearing oils. No complete analysis has been carried out by the refinery as far as is known, or in this laboratory, but knowing the source of the odorants, it was considered that the conclusions reached by Kalichevsky and Stagner (6) could be accepted as applicable to this investigation.

The odorant oil, according to the producers, is largely low boiling hydrocarbons containing 5-10% of sulfur as mercaptans, sulfides, and disulfides, together with some elementary sulfur.

According to Kalichevsky and Stagner (6), some of the sulfur compounds in the oils are corrosive to metals. Those immediately corrosive to metals are hydrogen sulfide, sulfur dioxide in the presence of moisture, relatively large amounts of free sulfur in oils free from mercaptans, or very small traces

of elementary sulfur in oil in the presence of mercaptans. Mercaptans themselves are not corrosive unless elementary sulfur is also present. Sulfides and disulfides are not corrosive.

They have suggested the following reactions to account for the effect of sulfuric acid on sulfur compounds usually found in petroleum distillates:

$$RSH + H_2SO_4 = RSHSO_3 + H_2O \qquad (1)$$

$$RSH + RSHSO_3 = (RS)_2SO_2 + H_2O \qquad (2)$$

$$(RS)_2SO_2 = R_2S_2 + SO_2 \qquad (3)$$

These reactions show that mercaptans are oxidized to disulfides, and the acid reduced to sulfurous acid in the process. In the presence of water the sulfur dioxide gives rise to sulfurous acid.

They also state that sulfur is produced from a side reaction, the reduction of H_2SO_4; that alkyl sulfides and alkyl disulfides and thiophenes are all relatively very soluble in fuming or 93% sulfuric acid, but only slightly soluble in the 75% concentration, and that hydrogen sulfide is oxidized by the 93% and stronger acids to free sulfur according to the following equation:

$$H_2S + H_2SO_4 = S + 2H_2O + SO_2 \qquad (4)$$

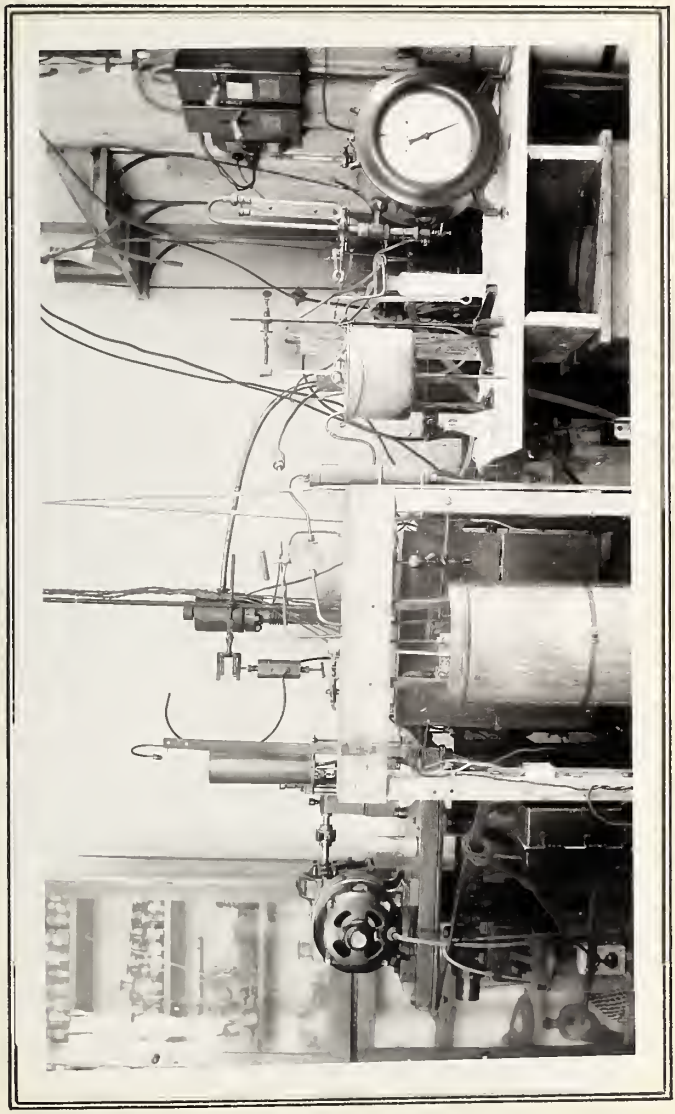
Sulfoxides and sulfones are similarily removed by their solubility in the 93% or stronger acids. Alkyl sulfates, formed during the reaction, are also removed by solution in the fuming

and 93% acids and to a lesser extent in the 73% concentration.

The principal consideration in this investigation is the formation of the sulfur dioxide (which was very noticeable in the off-gases) from the mercaptans.

PLATE 4

Showing the apparatus as illustrated in Figure IV. The compressor, storage system, and Bourdon-tube recording guage are not shown in this plate.



Experimental

Materials

The autoclave, shown approximately two-fifths size in Figure 5, was constructed of 18-8 Austenitic Chrom-nickel Alloy Steel. This alloy is not appreciably attacked by sulfuric acid in any concentration.

The metal, acid solutions, and mercury, were prepared as described in Part 1.

The natural gas was taken directly from the city gas mains and on analysis in the laboratory was found to be of the following composition by volume:

CH_4	.....	90.3 %
C_2H_6	.....	2.84%
N_2	.....	6.71%
CO	.....	0.15%

Sulfur analysis indicated a sulfur content of 6.48 grains per 100 cubic feet of gas, and was remarkably constant during the course of the experiments.

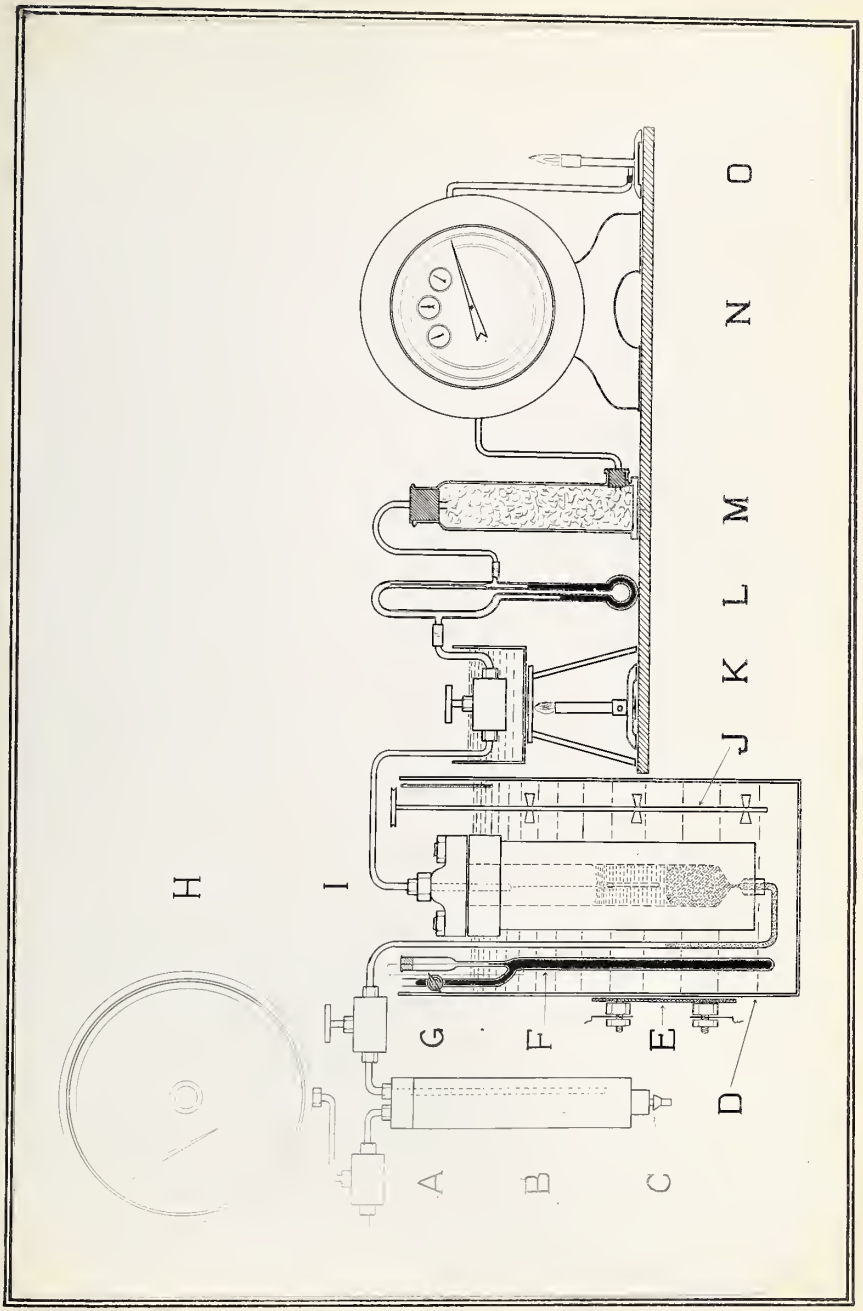
Apparatus

The high pressure apparatus was assembled as shown in Figure 5. A three-stage compressor capable of raising the pressure to 4,000 pounds was connected to a large gas storage tank, which in turn was connected to an auxiliary tank through a check valve. The auxiliary tank was connected by a three-way valve, A, to the

FIGURE 4

A .... Three-way connection
B .... Trap for mercury and acid
C .... Needle valve
D .... Thermostat
E .... Heater
F .... Thermoregulator
G .... Check valve
H .... Bourdon-tube recording guage
I .... Autoclave
J .... Stirrer
K .... Expansion valve
L .... Flow meter
M .... Soda-lime tower
N .... Sargent Wet Test Meter
O .... Platinum-tipped microburner

FIGURE 4



Bourdon-tube recording guage,H, and to the trap,B, which was fitted with a needle valve, C. The trap, B, was connected to the bottom of the autoclave through the check valve, G. From the top of the autoclave, I, the connection was made to a heated expansion valve, K, then to a flow meter, L, then through, M, a soda-lime tower which was connected to a Sargent Wet Test Meter, N. The outlet from the meter was attached to a platinum-tipped microburner, O.

The apparatus for controls at atmospheric pressure, was of the type described under hydrogen sulfide in Part II. In one set of experiments a connection in series was used, while in the second set, the parallel arrangement was used. The gas was taken from the gas line used in the laboratory for routine purposes.

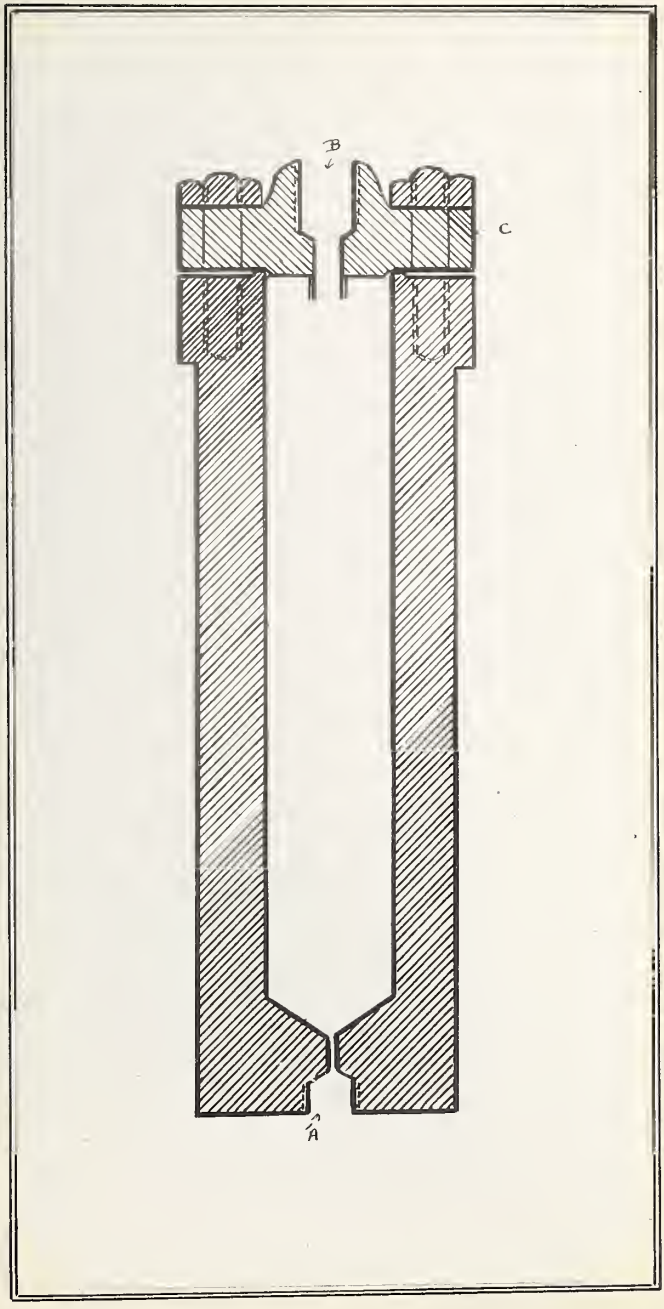
Analytical Methods

In the high pressure experiments, the apparatus was connected as shown in Figure 5. Mercury was poured into the autoclave to the height of one and a half inches as a seal between the steel connecting tubing and the acid. The volume of the acid solution which was added next was 150 cc. The lead sample was suspended in the acid by means of a glass hook attached to the autoclave head. The head of the autoclave was securely tightened in place and the valve, G, opened very

FIGURE 5

A .... 1/8 inch opening
B .... 3/16 inch opening
C .... The head - fastened
with six bolts.

FIGURE 5



slightly, allowing the gas from the auxiliary storage tank to fill the autoclave by bubbling through the acid solution. When the pressure in the autoclave reached equilibrium with that in the auxiliary tank, the expansion valve, K, slightly heated, was adjusted to the desired rate of flow, this being facilitated by the use of the flow meter, L.

The sample of metal was taken from the autoclave once in twenty-four hours, and after washing and drying, the change in weight was noted. Three to four days was considered sufficiently long to give an indication of the rate of reaction.

On completion of an experiment with one piece of metal, the acid was removed from the autoclave, a new solution was poured in and the metal changed. The autoclave was carefully cleaned before a new experiment was commenced.

During the progress of the action of the acid on the metal, analysis of the gases going into the autoclave and leaving it, were made for sulfur. The analysis was carried out on the following gases:

(1) the natural gas from the auxiliary tank or city main;

(2) the gas after it passed through the acid solution;

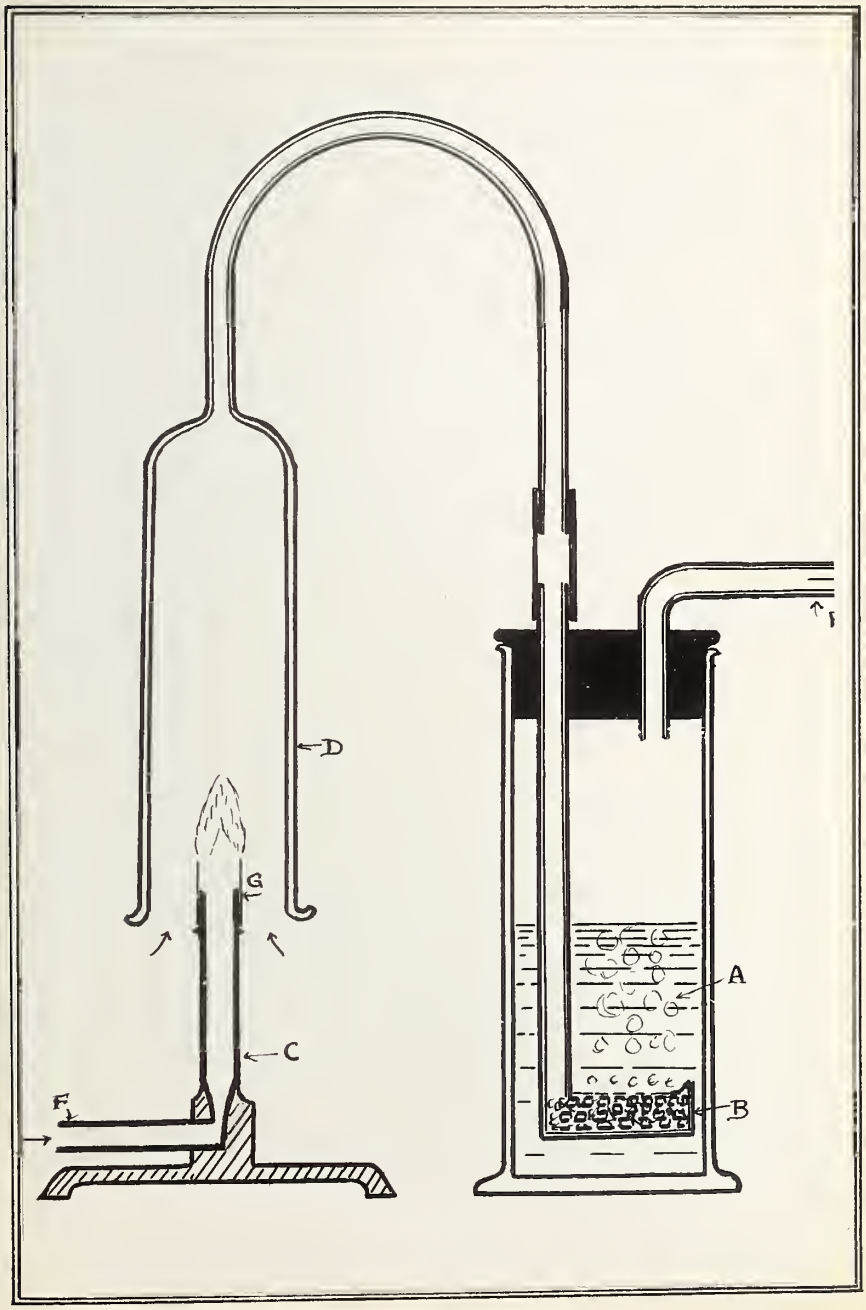
(3) the gas after it passed through the soda-lime tower.

Tests were also carried out on the gas after it passed through the acid for hydrogen sulfide, but no traces of the gas were

FIGURE 6

A .... Sodium carbonate solution
B .... Fritted glass filter
C .... Microburner
D .... Pyrex trumpet
E .... Connection to suction
F .... Connection to meter
G .... Platinum tip on burner

FIGURE 6



found using lead acetate. It was evident from the odor that SO_2 was present in the gas after acid washing and was completely absorbed by the soda-lime tower. Two complete sets of analyses were carried out on the gases during the observations on each piece of metal. The apparatus for sulfur analysis, preparation of reagents, and procedure, are based on the Reference's method, modified as described below:

Determination of Sulfur in Odorized Viking Natural Gas

Materials

Standard Sodium Carbonate. A pure sample of sodium carbonate was dried in an oven at 200°C., and a portion of this, equal to 1.6529 grams, was weighed out, and distilled water added to make up to 1,000 cc.

Standard Sulfuric Acid. The solution was prepared by diluting 62.6 cc. of a half normal acid solution to one liter. It was standardized against standard sodium hydroxide and checked against the sodium carbonate solution, then adjusted to exactly the same normality as the sodium carbonate.

Methyl Orange. The methyl orange was prepared by weighing out 0.003 gm. of methyl orange and making up to one liter. For convenience, it was kept in a liter wash bottle.

Apparatus

A diagram of the apparatus used is shown in Figure 6. A test meter as shown in, M, Figure 6, (graduated to 1/1,000 of a cubic foot) was connected to the microburner, C, placed beneath the pyrex glass trumpet, D. The trumpet, D, was connected by means of a short rubber tube to a fritted glass filter, B. This filter was fitted in such a manner that the gas leaves the filter, B, near the bottom of the sodium carbonate solution and passes upwards through it. The filter was securely fitted into the top of the collecting bottle by means of a rubber stopper. The bottle, A, was connected to a suction line. The suction pump was adjusted to draw all the products of combustion from the burner, together with some excess air, through the sodium carbonate solution, by observation of the behaviour of the flame.

The determination was made as follows: The water in the meter was kept saturated with gas by its continuous passage from the storage system. Before making the analysis, the meter was flushed with at least 0.2 cu. ft. of the gas to be analysed. The platinum-tipped microburner was connected by means of a rubber tube to the meter as shown in, O, Figure 6. The glass filter was then connected to the trumpet, the suction pump attached, the gas lighted, the burner quickly put in place,

and the products of combustion aspirated through the reaction bottle until 0.05 to 0.1 cu. ft. of gas was burned. The flame was then removed, the aspiration continued for about two minutes, and the apparatus allowed to cool to room temperature. The glass filter was then washed with a fine jet of water, the solution from the reaction flask was poured into a 100 cc. Nessler tube, the flask washed with water, and finally with 10 cc. of the methyl orange solution, the washings being added to the Nessler tube. The excess sodium carbonate was titrated with standard sulfuric acid to give the cubic centimeters of sodium carbonate converted to sodium sulfite. In carrying out the titration, two color controls were used: (1) 25 cc. of the sodium carbonate solution was added to a Nessler tube, 10 cc. of methyl orange, and water added to equal the volume of the titrated solutions. (2) 25 cc. of the sodium carbonate solution was titrated with 25 cc. of the acid solution - the color at the end point was used as the color control for the rest of the analyses. Using this method, it was found that error in color reading was negligible. After the controls were made, the actual analysis was proceeded with in the following order: First, gas after it had passed through the soda-lime tower; second, gas before it passed through the soda-lime but after passing through the acid; third, gas

drawn directly from the storage tank. This gas was drawn through the needle-valve, C, Figure 6.

In calculating the amount of sulfur present the following equation was used to give results in the usual units:

$$\text{Grains S per 100 cu. ft.} = \frac{\text{No. of cc. of } Na_2CO_3 \times 0.7716}{\text{Cu. ft. of gas used (N.T.P.)}}$$

The sulfur content of the gas before passing through the acid was found to be remarkably constant at nearly 6.5 grains per 100 cu. ft.

Results and Discussion

These experiments differed radically in some respects from those in Parts I and II. First, the amount of acid solution (150 cc.) was much larger in the pressure experiments than under atmospheric pressure. Second, the amount of sulfur, in the total volume of gas passed, was very much less than in the experiments in Part II. The experiments in this section, at atmospheric pressure, used the same volume of acid solution (30 cc.) as previously, but the second difference noted above, was true. However, despite the small amount of sulfur involved, the rate of corrosion was appreciably accelerated by the presence of the odorized gas.

From the data on the sulfur analysis, as shown in Tables XI and XII, it is evident that the sulfur compounds in the gas were almost completely converted to sulfur dioxide by the 93% acid, the extent of conversion decreasing with concentration. In the 37% concentration the amount converted was almost negligible. Tests for hydrogen sulfide showed negative results. It is possible that hydrogen sulfide is a primary product of the decomposition of mercaptans, but in the presence of acid, is immediately converted to a sulfur dioxide, sulfur, and water as in reactions (4) above, and (7) of Part

TABLE IX

Lead in Sulfuric Acid and Odorized Viking Natural Gas.

Temperature ..... Room Temp.
Pressure ..... Atmospheric.
Amount of Acid used ..... 30 cc.

The gas was passed through the five solutions with test tubes connected in series, passing through the 93%, 77%, 62%, 37% acid, and water, in the order named.

	Time	Wt. After	Change
Wt. of Sample 5.4977 gm.	9 hrs.	5.4839	-0.0138
Acid Conc.....93% .	21	5.4738	-0.0239
	45	5.4596	-0.0381
	75	5.4596	-0.0381
Wt. of Sample 5.2970 gm.	9 hrs.	5.2969	-0.0001
Acid Conc.....77% .	21	5.2969	-0.0001
	45	5.2966	-0.0004
	75	5.2965	-0.0005
Wt. of Sample 5.6175 gm.	9 hrs.	5.6174	-0.0001
Acid Conc.....62% .	21	5.6174	-0.0001
	45	5.6178	0.0003
	75	5.6181	0.0006
Wt. of Sample 5.4787 gm.	9 hrs.	5.4792	0.0005
Acid Conc.....37% .	21	5.4795	0.0008
	45	5.4802	0.0015
	75	5.4809	0.0022
Wt. of Sample 5.4351 gm.	9 hrs.	5.4357	0.0006
Water & Natural Gas.	21	5.4364	0.0013
	45	5.4374	0.0023
	75	5.4395	0.0044

- - - - - - -

TABLE X

Lead in Sulfuric Acid and Odorized Viking Natural Gas.

Temperature ..... Room Temp.
Pressure ..... Atmospheric.
Amount of Acid used ..... 30 cc.

The gas was passed through the five solutions with the test tubes connected in parallel - the flow was equalized by means of screw clamps on the rubber connections.

	Time	Wt. After	Change
Wt. of Sample 5.4375 gm.	9 hrs.	5.4184	-0.0191
Acid Conc.....93% .	18	5.4075	-0.0300
	27	5.4004	-0.0371
	51	5.3970	-0.0405
	75	5.3948	-0.0427
	7 days	5.3898	-0.0477
	32	5.3388	-0.0987
Wt. of Sample 5.4335 gm.	9 hrs.	5.4332	-0.0003
Acid Conc.....77% .	18	5.4330	-0.0005
	27	5.4328	-0.0007
	51	5.4326	-0.0009
	75	5.4328	-0.0007
	7 days	5.4328	-0.0007
	32	5.4314	-0.0021
Wt. of Sample 5.3854 gm.	9 hrs.	5.3855	0.0001
Acid Conc.....62% .	18	5.3855	0.0001
	27	5.3854	0.0000
	51	5.3853	-0.0001
	75	5.3853	-0.0001
	7 days	5.3864	0.0010
	32	5.3865	0.0011

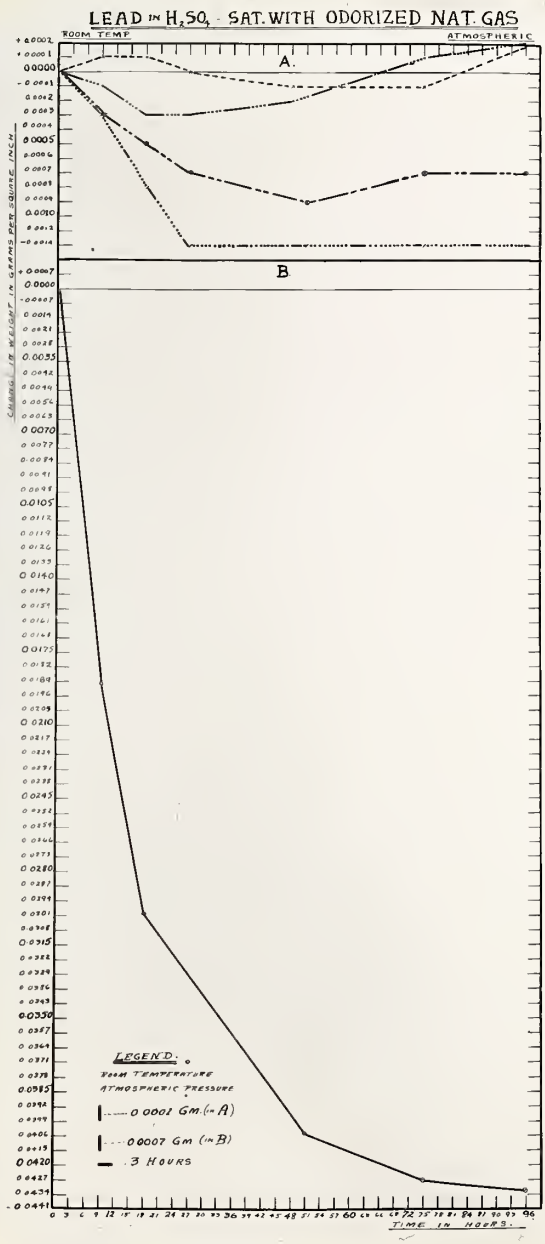
(Continued on next page.)

TABLE X (Cont'd)

	Time	Wt. After	Change
Wt. of Sample 5.4340 gm.	9 hrs.	5.4339	-0.0001
Acid Conc.....37% .	18	5.4338	-0.0002
	27	5.4338	-0.0002
	51	5.4339	-0.0001
	75	5.4341	0.0001
	7 days	5.4347	0.0007
	32	5.4358	0.0018
Wt. of Sample 5.4603 gm.	9 hrs.	5.4600	-0.0003
Water	18	5.4595	-0.0008
	27	5.4591	-0.0012
	51	5.4591	-0.0012
	75	5.4591	-0.0012
	7 days	5.4591	-0.0012
	32	5.4591	-0.0012
Wt. of Sample 5.4552 gm.	9 hrs.	5.4552	0.0000
In dry gas.	18	5.4552	0.0000
	27	5.4550	-0.0002
	51	5.4550	-0.0002
	75	5.4549	-0.0003
	7 days	5.4549	-0.0003
	32	5.4549	-0.0003

- - - - - - - -

FIGURE 14


LEAD IN H_2SO_4 - SAT. WITH ODORIZED NAT. GAS
ROOM TEMP
ATMOSPHERIC
A
B
CHANGE IN WEIGHT IN GRAMS PER SQUARE INCH
LEGEND:
ROOM TEMPERATURE
ATMOSPHERIC PRESSURE
0.0001 Gm. (in A)
0.0007 Gm (in B)
3 HOURS
TIME IN HOURS.

11. The production of sulfur dioxide, in all probability, follows the reactions (1), (2), and (3) shown above.

Table X, supplemented with observations from Table 1X, show the results obtained under atmospheric conditions. The data of Table 1X are not reliable for concentrations other than that of the 93% acid, since the gas passed through the acids in series, and was largely freed of sulfur in the first reaction vessel - the 93% acid. It may be observed in Figure 17, and Table 1X, that the rate of corrosion for the first twenty-four hours is only slightly less than the rates given in Part 11, where sulfur dioxide or hydrogen sulfide was the added agent of corrosion. Table X, and Figures 14 and 17, show a somewhat greater rate of corrosion in an equal period of time. Following the twenty-four hour period of corrosion, passivity sets in to some extent, as shown by a decreased rate of corrosion. Table X, shows that the rate changes only slowly for the next twenty-five days, the average being slightly greater than the rate between the second and the seventh day. It is suggested that the slow rate of corrosion after the first day is due to the limited supply of sulfur dioxide available as compared to the experiments in Part 11. The tabulated results show that the rate at the end of thirty-two days is considerably greater than that found with 93% acid alone. It is also shown in Table X,

TABLE XI

Lead in Sulfuric Acid and Odorized Natural Viking Gas

Temperature ..... 25°C.
Pressure ..... 1000 pounds.
Amount of Acid used ..... 150 cc.

		Time	Wt. After	Change
Wt. of Sample	5.4963 gm.	24 hrs.	5.4821	-0.0142
Acid Conc.....	93%.			
Volume of gas passed	134 cu. ft.			
Grains Sulfur per 100 cu. ft.....	6482	48	5.4617	-0.0346
Grains sulfur passed into acid ...	0.8686			
Grains S as SO_2 and unconverted ..	0.8065			
Grains S unconverted to SO_2	0.0000	72	5.4441	-0.0522
Grains S passed out as SO_2	0.8065			
Grains S retained by acid	0.0621			
Wt. of Sample	5.1820 gm.	24 hrs.	.....	.....
Acid Conc.....	77%.			
Volume of gas passed	166 cu. ft.			
Grains Sulfur per 100 cu. ft.....	6482	48	5.1816	-0.0004
Grains S passed into acid	1.0759			
Grains S as SO_2 and unconverted ..	0.9478			
Grains S unconverted to SO_2	0.0949	72	5.1811	-0.0009
Grains S passed out as SO_2	0.8529			
Grains S retained by acid	0.1281			

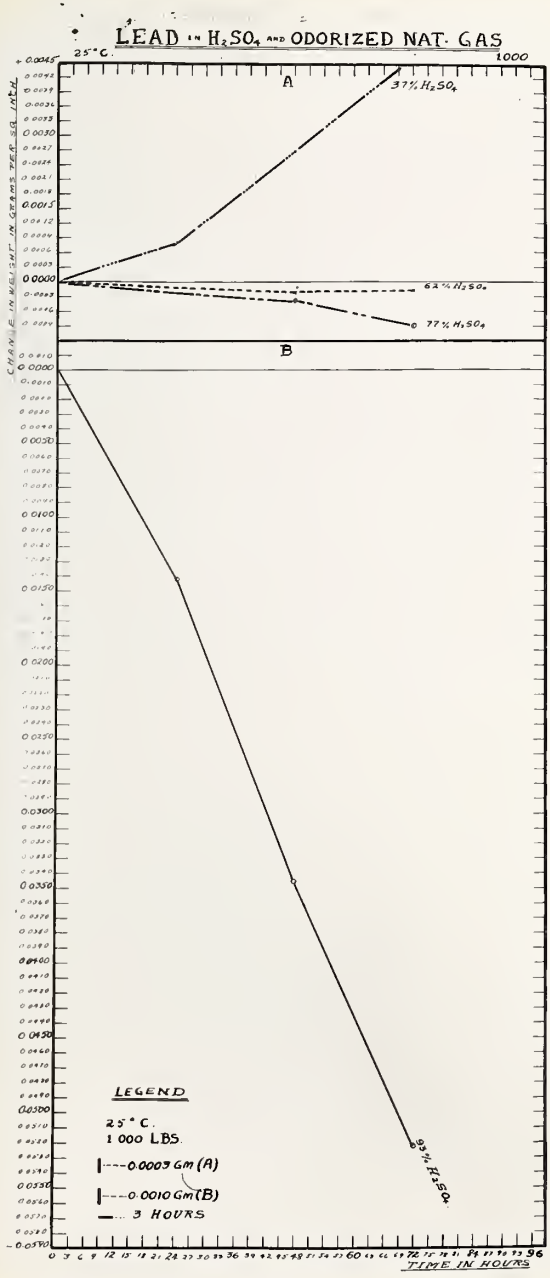
(Continued on next page.)

TABLE XI (Cont'd.)

		Time	Wt. After	Change
Wt. of Sample	5.5098 gm.	24 hrs.	.....	.....
Acid Conc.....	62%.			
Volume of gas passed	145 cu. ft.			
Grains Sulfur per 100 cu. ft.....	6482	48	5.5096	-0.0002
Grains S passed into acid	0.9399			
Grains S as SO_2 and unconverted ..	0.8504			
Grains S unconverted to SO_2	0.8068	72	5.5096	-0.0002
Grains S passed out as SO_2	0.0436			
Grains S retained by acid	0.0895			
Wt. of Sample	5.2568 gm.	24 hrs.	5.2576	0.0008
Acid Conc.....	37%.			
Volume of gas passed	125 cu. ft.			
Grains Sulfur per 100 cu. ft.....	6482	48	.....	.....
Grains S passed into acid	0.8103			
Grains S as SO_2 and unconverted ..	0.7330			
Grains S unconverted to SO_2	0.6945	72	5.2616	0.0048
Grains S passed out as SO_2	0.0385			
Grains S retained by acid	0.0773			

- - - - - - - -

FIGURE 15


LEAD IN H_2SO_4 AND ODORIZED NAT. GAS
25° C.
1000
A
37% H_2SO_4
62½% H_2SO_4
77% H_2SO_4
B
93% H_2SO_4
CHANGE IN WEIGHT IN GRAMS PER SQ. INCH
TIME IN HOURS
LEGEND
25° C.
1 000 LBS.
---0.0003 Gm (A)
---0.0010 Gm (B)
3 HOURS

that the 77% solution behaves, initially, like 77% solution where sulfur dioxide was added, but the sudden increase in the rate of corrosion does not occur as it did with the same concentration and sulfur dioxide. It is probable that the behaviour with natural gas would have duplicated that with sulfur dioxide if sufficient gas had been passed to supply an equivalent amount of sulfur dioxide.

The rate of corrosion under pressure, as given in Table XI, Figure 15, for 1,000 pounds per sq. inch, and in Table XII, Figure 16, for 3,500 pounds per sq. inch, was of considerable interest. The graphs of Figure 17, show that the rates under pressures of 1,000 and 3,500 pounds are practically the same for the 93% acid. Compared to the data of Table X, the rate is initially less, but definitely greater at the end of three days. Compared to experiments with sulfur dioxide, (Table VI) the rate of corrosion is only one-half to one-third as great. It may again be said that the amount of sulfur in the gas is the determining factor. Considering the small amount of sulfur added, the corrosion is relatively large, and suggests that pressure has an appreciable effect in the presence of sulfur dioxide.

It would be interesting to carry out these experiments using the same quantity of acid in each case, and the same rate

TABLE XII

Lead in Sulfuric Acid and Odorized Natural Viking Gas

Temperature ..... 25°C.
Pressure ..... 3500 pounds.
Amount of acid used ..... 150 cc.

		Time	Wt. After	Change
Wt. of Sample	5.2731 gm.	24 hrs.	5.2568	-0.0163
Acid Conc.....	93%.			
Volume of gas passed	221 cu. ft.	48	5.2355	-0.0376
Grains Sulfur per 100 cu. ft.....	6482			
Grains S passed into acid	1.4325	72	5.2180	-0.0551
Grains S as SO_2 and unconverted ..	1.3302			
Grains S unconverted to SO_2	0.0000	96	5.1995	-0.0736
Grains S passed out as SO_2	1.3302			
Grains S retained by acid	0.1023			
Wt. of Sample	5.2585	24 hrs.	5.2586	0.0001
Acid Conc.....	77%			
Volume of gas passed	254 cu. ft.	48	.....	.....
Grains S per 100 cu. ft.....	6482			
Grains S passed into acid	1.6465	72	5.2579	-0.0006
Grains S as SO_2 and unconverted ..	1.4503			
Grains S unconverted to SO_2	0.1453	96	5.2583	-0.0002
Grains S passed out as SO_2	1.3050			
Grains S retained by acid	0.1962			

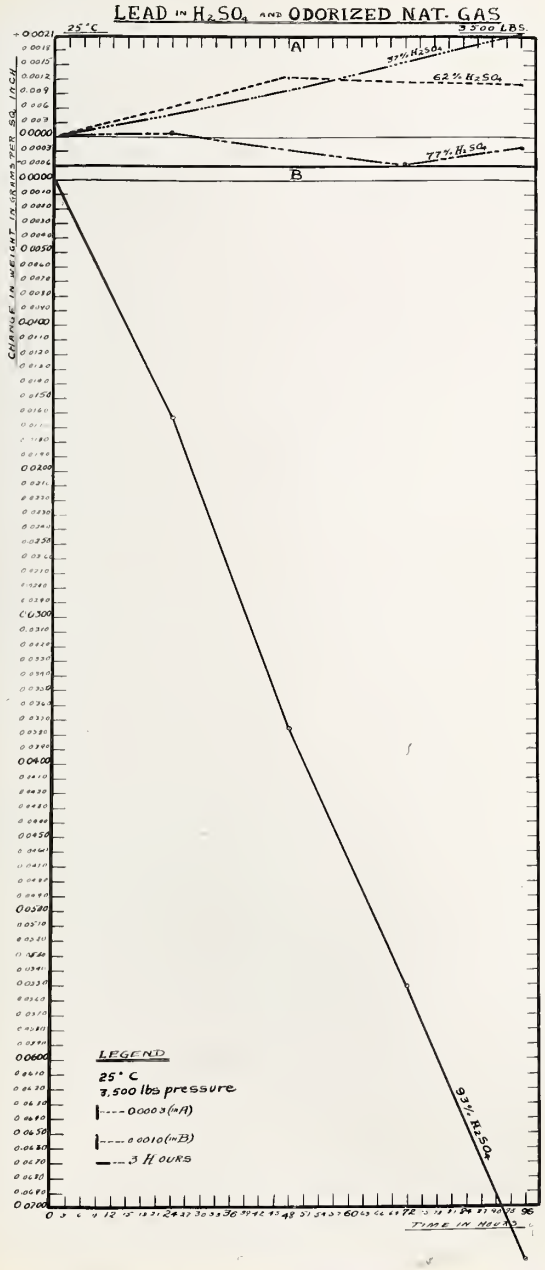
(Continued on next page.)

TABLE XII (Cont'd.)

		Time	Wt. After	Change
Wt. of Sample	5.1941 gm.	24 hrs.	.....	.....
Acid Conc.....	62%			
Volume of gas passed	276 cu. ft.	48	5.1954	0.0013
Grains S per 100 cu. ft.....	.6482			
Grains S passed into acid	1.7825	72	.....	.....
Grains S as SO_2 and unconverted ..	1.6190			
Grains S unconverted to SO_2	1.5320	96	5.1952	0.0011
Grains S passed out as SO_2	0.0870			
Grains S retained by acid	0.1635			
Wt. of Sample	5.0315 gm.	24 hrs.	.....	.....
Acid Conc.....	37%			
Volume of gas passed	270 cu. ft.	48	5.0325	0.0010
Grains S per 100 cu. ft.....	.6482			
Grains S passed into acid	1.7501	72	.....	.....
Grains S as SO_2 and unconverted ..	1.5835			
Grains S unconverted to SO_2	1.5008	96	5.0337	0.0022
Grains S passed out as SO_2	0.0827			
Grains S retained by acid	0.1666			

- - - - - - - -

FIGURE 16


LEAD IN H_2SO_4 AND ODORIZED NAT. GAS
25°C
3500 LBS.
A
B
77% H_2SO_4
62% H_2SO_4
77% H_2SO_4
93% H_2SO_4
CHANGE IN WEIGHT IN GRAMS PER SQ. INCH
TIME IN HOURS
LEGEND
25° C
7,500 lbs pressure
0.0003 (in A)
0.0010 (in B)
3 HOURS

of gas flow, while extending the period of observation sufficiently to ensure that the sulfuric acid was saturated with sulfur dioxide.

Although the amount of sulfur in the odorants of the gas was relatively low, yet the rate at the end of four days was six times that under atmospheric conditions with no sulfur dioxide present, and approximately three and a half times as rapid as results obtained under similar pressure but lacking the sulfur dioxide in the acid. This can be gathered from the results illustrated in Figure 17.

In the lower concentrations of acid, the rates are comparable to those where pressure alone was used (as discussed in Part 1). Very slight corrosion occured in the 77%, 62%, and 37% acid at any pressure, during the four days observed. The explanation offered is the same as given earlier, that the amount of sulfur available was too small to raise the concentration of sulfur dioxide in the acid to the value required for corrosion.

The question was raised as to the possibility of a galvanic action occuring, since the acid was in contact with the autoclave. In order to obtain some data on such an effect, if any, and to obviate the necessity of lining the autoclave with acid-proof material, (glass was tried, but the gas followed

TABLE XIII

18-8 Austenitic Steel and Lead in Contact with It

Temperature ..... 25 degrees C.
Pressure ..... 3500 pounds.
Amount of acid used ..... 150 cc.

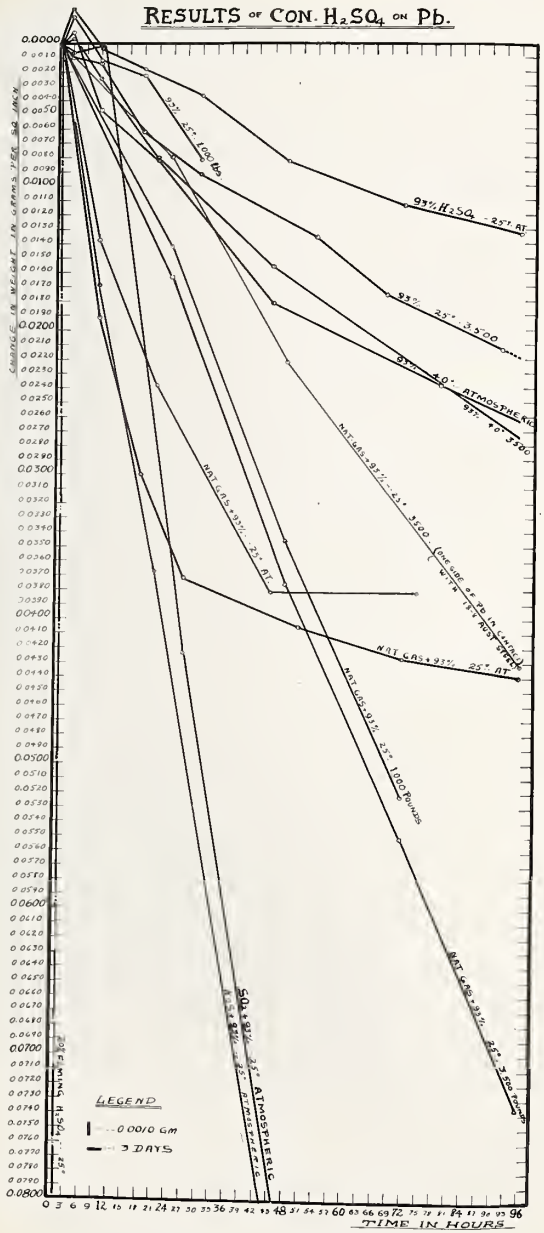
Austenitic Steel	Time	Wt. After	Change Per Sq. Inch
Wt. of Sample 12.4430 gm.	24 hrs.	12.4430	0.0000
Surface area 3 sq. inches	48	12.4428	-0.0001
Acid Conc... 93%	72	12.4427	-0.0001
	96	12.4426	-0.0001
Austenitic Steel & Lead			
Wt. of Aust. Steel 12.4426	24 hrs.	12.4362	-0.0021
Surface area ..... 3 sq. in.	48	12.4272	-0.0051
Acid Conc..... 93%	72	.....	.....
	96	12.4118	-0.0103
Wt. of Lead 5.5119 gm.	24 hrs.	5.5039	-0.0080
Surface area 1 sq. inch	48	5.4907	-0.0212
Acid Conc... 93%	72	.....	.....
	96	5.4687	-0.0432
Austenitic Steel Continued Alone			
Wt. of Aust. Steel 12.4118	24 hrs.	12.3968	-0.0050
Surface area ..... 3 sq.in.	48	12.3739	-0.0126
Acid Conc..... 93%	72	12.3500	-0.0206
Austenitic Steel Continued Alone after Treating with Fuming HNO_3			
Wt. of Aust. Steel 12.3492	24 hrs.	12.3358	-0.0044
Surface area ..... 3 sq. in.			
Acid Conc..... 93%			

- - - - - - -

Acid changed for each series of runs.

- - - - - - -

FIGURE 17


RESULTS OF CON. H_2SO_4 ON Pb.
CHANGE IN WEIGHT IN GRAMS PER SQ INCH
TIME IN HOURS
93% 25° 100 lbs
93% H_2SO_4 - 25° AT.
93% 25° 3500
93% 40° ATMOSPHERIC
93% 40° 3300
NAT GAS + 93% 25° 3300 (one side of Pb in contact with acid)
NAT GAS + 93% 25° AT.
NAT GAS + 93% 25° AT.
NAT GAS + 93% 25° 1000 Pounds
NAT GAS + 93% 25° 3300 Pounds
SO_4 + 93% 25° ATMOSPHERIC
LEGEND
0.0010 Gm
3 DAYS

the wall of the autoclave instead of passing directly through the mercury, and the facilities for other methods of insulation were lacking or would have made the results probably as doubtful), it was decided to observe the rate of corrosion on alloy steel of the same composition used in the manufacture of the autoclave, namely, 18-8 Austenitic Chrom-nickel Alloy Steel.

The results of the observations are shown in Table XIII. For the first four days the corrosion of the metal was negligible in the 93% acid. A slight decrease in weight, as shown in Table XIII, suggested that corrosion was slow, at first and would increase with time. Following the four day test, a piece of lead, of size and shape used in previous experiments, was placed in contact with the alloy steel. The conditions as to pressure, and the rate of gas flow were the same as those prevailing when lead alone was in the acid solution.

The plotted results, Figure 17, indicate that corrosion was not the result of galvanic action between the lead and the alloy steel. The actual amount of corrosion of the lead indicates that nearly half of the surface of the lead was taken out of direct contact with the acid - this may be assumed to be the surface in contact with the alloy steel. Had galvanic action taken place in any of the reactions, during the series of experiments, the logical concentration to show this galvanic

effect would have been the 37% concentration, but nothing in the data on this concentration suggests that galvanic action had been a factor in the observed corrosion.

Finally, the rate of corrosion in its relation to the life of lead gaskets in the high pressure sulfuric acid scrubbers is of interest. The observed rate, in Tables XI and XII, for the 93% acid gives a rate of penetration of approximately 0.0001 inches per day for the first three days. Expressed otherwise, this is 0.0003 gm. Pb. per sq. cm. per day. These rates are much less (one-fourth or so), than the rates in the scrubbers. The fact that corrosion products protect the gaskets to a greater extent makes the discrepency even more pronounced. However, the corrosion observed in the gaskets is after periods of one hundred to two hundred days, and extrapolation from an effect obtained over three or four days is hardly justified. It may be suggested that during this longer period of time, the acid becomes saturated with sulfur dioxide, resulting in increased corrosion over that found in the controlled conditions.

Summary and Conclusions

It was found that sulfur dioxide was one of the products formed when odorized natural Viking gas was passed through sulfuric acid. Tests did not reveal the presence of any hydrogen

sulfide in the off-gases.

On the whole, only slight difference seems to exist as to the influence of pressure on the rate of corrosion, under the conditions existing in this series of experiments. It is probable that experiments under pressure, for longer periods of time, would show this difference to a greater extent.

From the data obtained, it seems definite that the corrosion of the lead gaskets in the sulfuric acid gas pressure scrubbers was due to the action of sulfur dioxide under high pressure.

General Discussion

Visual inspection and theory suggested that corrosion of lead by sulfuric acid produced lead sulfate as the final product, with small amounts of sulfur being included in the precipitate.

Analysis of the precipitates, which were principally from experiments with acids of high concentration, and prolonged reaction, showed the following percentages of sulfur present:

20% fuming sulfuric acid ..... 1.50% S.

93% sulfuric saturated with SO_2 ..... 0.89% S.

93% sulfuric saturated with nat. gas ... 8.00% S.

93% sulfuric acid ..... 2.50% S.

Lack of precipitated material did not permit analysis in duplicate and the results of 8.0% and 2.5% may be questioned due to the limited amount of precipitate available for analysis.

The per cent sulfur present was determined by volatilizing the sulfur from a weighed quantity of dried precipitate.

Qualitative analysis for sulfur was made by extracting the sulfur with benzene and evaporating the solvent. A yellow residue was left in the evaporating dish, which on ignition produced copious amounts of sulfur dioxide. As another qualitative test for sulfur in the fuming acid, we may consider the formation of the blue coloration as indicative of the

formation of free sulfur.

Tests were carried our for lead sulfite by using dilute sulfuric acid on the precipitates. These tests showed negative results.

The corrosion was most pronounced in pits. It also appeared to be intercrystalline, along gliding planes and cleavage faces, but sufficient microscopic work was not carried out to make it conclusive. The sharp edges did not appear to be attacked to any appreciable extent after long periods of time, as for example, the eighty-four day corrosion in the 93% sulfuric acid saturated with sulfur dioxide. The corrosion appeared to be remarkably uniform over the entire surface. No evidence of increased or decreased corrosion was observed at the points of rest, or along the margin of the hole which was punched in the metal for the purposes of suspension or removal. It was observed that the part of the metal protected by the precipitate at the bottom of the reaction vessel (atmospheric) showed a decreased rate of corrosion. This was illustrated to advantage in the 20% fuming acid, where, after a period of two weeks the upper part was nearly entirely corroded away while the lower portion showed a considerable thickness of metal.

General Conclusions and Summary

Pressure shows a definite increase in the rate of corrosion in sulfuric acid, especially in the 93% concentration.

Corrosion rate is increased by the presence of sulfur dioxide or hydrogen sulfide.

Reactions are appreciably accelerated in acid solutions containing sulfur dioxide, if pressure is an added factor.

The rate of corrosion under atmospheric conditions appears to be directly dependent on the amount of water present in the acid. It may be postulated that corrosion of lead in sulfuric acid is directly proportional to the acid concentration, and may be represented as follows:

$H_2SO_4.SO_3 > H_2SO_4(SO_2) > H_2SO_4 > H_2SO_4\text{-}H_2SO_3 > H_2SO_3$ - with the rate of reaction being accelerated under the influence of pressure.

- - - - -

Acknowledgement

The author takes this opportunity to express his sincere thanks to Dr. E. H. Boomer for his assistance, kindly advice, and the use of the high pressure apparatus, during the course of this investigation. He also wishes to thank the members of the staff of the Chemistry Department, and others, who may have offered helpful suggestions, or in any way assisted in bringing this work to a conclusion.

References

(1) Ditz, H. and Kanhauser, F., Zeit. anorg. Chem., 98, 128, 1916.

(2) Donk, A. D., Chem. Weekbl., 13, 92, (1916).

(3) Fresenius, C. R., Liebig's Ann., 59, 125, (1846).

(4) Freundlich and Scholz, Koll. Beih., 16, 234, (1923).
Colloids, H. R. Kruyt, (John Wiley & Son)

(5) Gladstone, J. H. and Hibbert, W., (5) Phil. Mag. (5), 31, 42, (1891).

(6) Kalichevsky, V. A. and Stagner, B. A., Chemical Refining of Petroleum, (The Chemical Catalog Co.), (1933).
Also A. E. Wood, A. Lowy, and W. F. Garagher: Ind. Eng. Chem., 16, 1116-20, (1924).
A. E. Wood, C. Sheely, and A. Q. Trusty,: Ind. Eng. Chem., 18, 169-71, (1926).
H. T. Bennet, and Le R. C. Story: Oil and Gas Journ., 25, No. 46, 162, (1927).

(7) Kolb, J., Dingler's Journ., 209, 268, (1873).

(8) Krase, N. W. and Goodman, J. B., Chem. and Met. Eng., 36, 162, (1929).

(9) Lambert, B. and Cullis, H. E., J. C. S., 105, 210, (1915).

(10) Marshall, A., Journ. Soc. Chem. Ind., 21, 1505, (1902).

(11) Mellor: A Comprehensive Treatise on Inorg. and Theoretical Chemistry, (Longmans and Co.), Vol. X, p.34.

(12) Mellor: ibid., Vol. X, p. 303.

(13) Ostwald, W., Principles of Inorg. Chem., (MacMillan & Co.) 1914

(14) Pleissner, Internat. Crit. Tables, (McGraw-Hill), Vol. VII, 318.

(15) Shipley, J. W., Journ. Soc. Chem. Ind., 41, 314, T, (1922)

(16) Whitney, W. R., J. A. C. S., 25, 394, (1903).

B29742